

FUELS 1924 - 1940

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ABSTRACT

The period 1924-1940 may be characterized as the flowering era of fuel science and technology. In the field of combustion this period saw the extensive development of the burning of pulverized coal under slagging conditions to generate steam; a greatly improved understanding of the kinetics and mechanism of the combustion of solid fuels. Coal gasification technology was advanced: by the development of gasifiers using oxygen; by operating at elevated pressure, under slagging conditions, and with a fluidized bed; and by demonstrating the feasibility of hydrogasification. During the period the efficient by-product coke oven almost completely replaced the beehive oven for producing metallurgical coke. Coal liquefaction and solvation progressed from the laboratory to the full-scale commercial plant. The Fischer-Tropsch process was discovered just prior to the period under discussion and it too progressed to the commercial stage during this period. Major advances were made in knowledge of the kinetics and mechanism of the oxidation of gaseous fuels and in knowledge of the properties of fuel-air mixtures. Extensive work was done on the chemical constitution of coal and tar and on their physical properties. This latter work led to the establishment of many ASTM standards. These impressive accomplishments in fuel science and technology are discussed in more detail in the paper.

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INTRODUCTION

In discussing fuels 1924-1940 we cannot isolate this first period of the symposium from preceding developments in fuel science and technology. Accordingly, an attempt will be made to summarize, briefly, the history of the field prior to 1924. In this way we can give perspective not only to the period under discussion but also we can establish a base on which subsequent developments have been built.

The subject of fuel is so broad, covering as it does solid, liquid and gaseous fuels, that it is obvious that we will have to limit both the scope and depth of our summary.

In the period under discussion, 1924-1940, which we will refer to as "our period," the interests of the Fuel Chemistry Division followed the content of the section in Chemical Abstracts then entitled, "Fuels, Gas, Tar and Coke." This then suggests that this be the scope of our discussion insofar as the basic fuels are concerned. Thus petroleum and its products are eliminated from our discussion which is logical not only because petroleum has not been one of the basic concerns of the Division of Fuel Chemistry but also because that fuel is the basic concern of the Division of Petroleum Chemistry.

Insofar as the depth of our discussion is concerned the major emphasis will be placed on carbonization, combustion, gasification and hydrogenation. In these fields key developments will be individually referenced. No attempt will be made to document all developments by a comprehensive bibliography but rather reference will be made to pertinent books and reviews containing such bibliographies (1-6). One of these (4) contains a comprehensive list of books on fuel science and technology covering the field prior to 1943.

Obviously, to keep our discussion manageable, it was necessary to eliminate many important areas of coal research. These are covered thoroughly by Lowry (4) and include such subjects as: coal petrography; the physical properties of coals; the chemical constitution of coal as determined by reaction with various compounds; the occurrence of sulfur, nitrogen and mineral matter in coal; ash fusion; the action of solvents on coal; and changes in coal during storage. I believe it is clear that meaningful discussion could not be given to such a wide range of topics. For detailed information on developments on these and other related fields in our period Lowry's book (4) should be consulted.

BRIEF HISTORY OF FUEL SCIENCE AND TECHNOLOGY

In considering the development of fuel science and technology prior to 1924, a logical and identifiable starting point is the year 1350 when coal first became a commercial commodity. Gas was first recognized as a state of matter in 1620 and coal was first distilled in the laboratory to yield gas in 1660.

The carbonization of coal to produce metallurgical coke was known in the late 1600's but was not practiced on a large scale until 1730. Coke was a by-product of another process developed in 1792 in which coal was distilled in an iron retort to

produce illuminating gas. These two processes initially were considered basically different and this concept persisted until the early 1900's.

With the increasing use of by-product coke ovens in the early 1900's, it became apparent that it was more efficient and economical to produce gas in the by-product coke oven than in the more labor intensive gas retort. The first by-product coke ovens were constructed in France in 1856. Since then they have gradually replaced beehive ovens which in 1900 accounted for about 95% of United States production but less than 5% in the late 1930's.

In 1855 Bunsen invented the atmospheric gas burner which opened the way for gas to expand its markets from lighting to a wide range of heating applications. The need for a high illuminating power for gas was no longer required after Welsbach invented the incandescent mantle in 1884. This need would have been eliminated anyway in a few years when the incandescent electric light was invented and the gas lighting load was eventually lost.

The advent of electric lighting opened up a great potential for coal combustion in the generation of steam for power generation. Thus, the combustion of coal went through the stages of burning in open-fireplaces in the early days to burning in the fuel beds of small household furnaces and subsequently large industrial furnaces and finally to burning as pulverized fuel in large central station furnaces. This latter application was first tried in 1876 but was not successful in the United States until the factors affecting proper furnace design were elucidated in 1917.

As the use of coal gas developed, the production of gas for heating purposes was also developing. The first gas producer making low Btu gas was built in 1832. This principle was not widely used until it was applied by the Siemens brothers in connection with their invention of the open hearth furnace in 1861. The use of producer gas increased from that time, until at the turn of the century it was an important factor for heating furnaces. But subsequent to that time its use has declined and in 1920 there were only 11,000 producers in use in the United States.

Another development in the field of gas making stemmed from Fontana's discovery in 1780 of the production of blue gas when steam was passed over incandescent carbon. This discovery was dormant until the period between 1823 and 1859 when additional experimental work was done on the steam carbon reaction. This eventually led to the development of processes for producing blue water gas in the period of 1859 to 1875. The first successful commercial process was developed by Lowe in 1875 when he introduced the carburetted water gas set. The increased use of this gasification technology continued until natural gas supplanted manufactured gas.

The history of coal hydrogenation begins in 1913 when work on the Bergius concept of direct hydrogenation of coal under hydrogen pressure at an elevated temperature was undertaken in Germany. A 31 ton per day pilot plant was built in Germany in 1921 and this brings us up to our period.

The possibility of producing liquid hydrocarbons from water gas (Fischer-Tropsch synthesis) was conceived in 1913. The first experimental work on this synthesis which is sometimes referred to as the indirect hydrogenation of coal was published in 1923 just prior to the beginning of our period.

This brief review of the major areas of application of fuel technology—combustion, carbonization, gasification and hydrogenation—presents a broad picture of the status of technology prior to 1924. As each individual area is discussed more specific details of the status of significant developments will be presented.

CARBONIZATION

General

The carbonization of coal involves the interaction of a wide range of chemical and physical properties of the coal itself in a high temperature thermal environment to produce a combustible gas, hydrocarbon liquids or tar and coke. The nature of the tar and its yield as well as the physical properties and reactivity of the coke and its yield are affected by the coal used and by the carbonizing conditions. Thus an understanding of the complex coal carbonization process involves research on: the plastic, agglutinating, agglomerating and swelling properties of coals; dependence of yields of products on type of coal, temperature and rate of heating; the chemical nature of coal tar; and as stated above the physical properties and reactivity of coke.

We cannot go into detail in these areas but we will try to indicate through summaries and selected examples of some of the developments in our period. Also it is only possible to mention here such important related areas (4) as: the properties of coke-oven gas; light oil from coke-oven gas; removal of sulfur compounds and miscellaneous constituents from coke-oven gas; and the treatment of ammoniacal liquors. Finally the broad field of industrial coal carbonization can only be covered by references (2,7) which review the status of the technology up to the end of our period.

The Plastic Properties of Coal

When caking coals are heated they undergo chemical transformations during which gases and condensable vapors are evolved leaving a solid residue consisting predominantly of carbon. During this process the coal softens, becomes more or less plastic and forms a bubbly compact mass which swells and then resolidifies leaving a porous solid known as coke.

The characteristics of coal in the plastic state were studied both extensively and intensively and the results of these studies have been summarized in considerable detail by Brewer (8).

The dilatometer (9-13) which measures the variations in the length of a confined coal sample heated at a definite rate gives the most complete information on the behavior of coal in the pre-plastic range (14).

Plastometers measure the fluidity or "viscosity" of coal in the plastic range. The constant torque (Geisler) plastometer (15) gives a better index of fluidity (14) and the variable torque (Davis) plastometer (16) allows the temperature at the softening point and the resolidification point to be determined with a high degree of accuracy.

It was first shown in 1870 (17) that those coals producing the best cokes were capable of incorporating a higher admixture of inert material than those coals producing inferior cokes. This observation led eventually to the development of test methods to measure the agglutinating value of coal. The more important of these were critically reviewed in 1929 by Marshall and Bird (17) who developed an updated method for measuring the agglutinating value of coal. Their work along with that of others (18,19) led ultimately to an A.S.T.M. Standard for measuring agglutinating value.

The agglomerating properties of coal indicate the tendency of the particles to stick to one another during heating. Work on this property (21-23) led eventually to the establishment of standard methods (24,25) for determining the free swelling index which is a measure of the agglomerating characteristics of a coal.

The swelling of coal during carbonization, if excessive, can lead to serious damage to the walls of the coke oven. Much work was done in this area (8) but no standard method was developed in our period for determining this characteristic. Work by the Bureau of Mines on sole-heated ovens (26) and vertical-slot ovens (27) afforded a satisfactory means for determining the expanding properties of coal (14).

Carbonization Tests

In discussing the experimental carbonization of coals, Reynolds (14) states "A large number of assays for determining the coke- and byproduct-making properties of coal have been developed but these methods give little information concerning the quality of products because of the small amount of sample carbonized. In 1929 the Bureau of Mines, in cooperation with the American Gas Association, developed a carbonization test (28) using charges weighing up to 200 pounds. The yields of coke and byproducts from this test are large enough to be tested by standard methods, thereby affording more complete data than are obtainable from tests on a smaller scale. Forty-eight coals have been carbonized by this method at high, medium, and low temperatures, and the qualities of the cokes and byproducts determined. Petrographic, agglutinating, plastic, expanding, friability, slacking, and oxidizing properties of these coals have been studied also. The comparison of test results and plant data (available for some coals) is an important part of this work and the agreement has been close enough fully to justify confidence in the method of test. Referring to the results of these investigations, Mulcahy wrote: (29) "Although much work on coal has been regarded as too fundamental or theoretical to be of practical value, the work of the Bureau of Mines in this respect is of tremendous value in indicating the trends we can expect under different carbonizing conditions."

The subject of this section was also reviewed in detail by Davis (30).

Physical Properties and Reactivity of Coke

The physical properties of coke such as density, size, distribution and strength as determined by the shatter, tumbler and other tests are significant in relation to the use of coke in fuel beds. Work in this area for our period has been reviewed by Mayers (31).

The "reactivity" of coke is (32) "somewhat loosely used to express the ability of a coke to interact with, usually, oxygen, carbon dioxide or steam." In his review of work on reactivity for our period Mayers (31) points out that it is not necessary to determine reactivities with various agents because "By comparing series of cokes of different reactivities, it has been shown that the reactivity with air is parallel to the ignition point (33) and the reactivity to carbon dioxide (34) and steam (35) is parallel to change in the ignition point; that the reactivity to air, to oxygen, and to carbon dioxide is parallel to changes in the ignition temperature (36-38); and that reactivities to air, to oxygen, to carbon dioxide, and to steam are all parallel (39,40). In view of this no attempt will be made here to review reactivity tests. Instead certain data from such tests will be considered in connection with the discussion of gasification reactions.

Coal Tar

Coal tar is one of the primary products of coal carbonization. It is a complex mixture containing principally aromatic compounds many of which are polynuclear. In our period some 348 compounds were identified as coming from the carbonization of

coal (41). Most of these appeared in the tar. The reference just mentioned also contains information on the effect of kind of coal and carbonization temperature on the characteristics and yield of coal tar and more detailed information on certain of the individual chemical constituents of the tar.

COMBUSTION

General

Studies of the combustion of solid fuels have involved experiments: with graphite, coal and wood charcoal; with sizes ranging from less than 200 mesh particles to 1" spheres; with individual particles, clouds of particles, filaments; and with both stationary and moving fuel beds. This wide range of conditions can be considered as falling into one of two categories—basic studies and studies of combustion processes. The former includes studies with graphite in filaments or in simple geometric shapes. The latter embraces coal in the more complex systems.

Basic Studies

At the beginning of our period (1924-1940) it had already been established that CO and CO₂ were produced together (42) in the reaction of carbon with oxygen. The work of Rhead and Wheeler (43) indicated that CO was the primary product at temperatures above 1000°C. Whereas the work of Langmuir and others (44-46) involving electrically-heated filaments at low pressure indicated that CO₂ was the main product. Work toward the end of the period showed that low pressure filament results were not valid because thermions upset the initial equilibrium of the primary reaction (47). Confirmation of the results of Rhead and Wheeler resulted from high velocity experiments (48) toward the end of the period. Thus in our period we saw the resolution of the primary product of the reaction between carbon and oxygen.

According to Nicholls, (49) "the chemistry of combustion and its physics as regards to 'temperature, time and diffusion' were well understood in 1840, (50) but such knowledge was not well disseminated." In light of this it is interesting to note that early in our period it was recognized (51-53) that the rate of combustion reactions was limited by the rate at which oxygen could be transported to the reacting surface. This conclusion was supported by experimental work (54,55) on the rate of oxidation of spheres of graphite which showed (56) "that the rate of the specific surface reaction depended strongly on the temperature at low temperatures (55) but less so at high ones; (54,55) that it was directly proportional to the oxygen concentration in the gas flowing over the carbon surface; (55) that it depended on approximately the 0.4 power of the mass velocity of the gas at high temperatures; (54,55) and that, for small particles, it was approximately inversely proportional to the diameter of the particle (54). Similar effects were found for the reduction of carbon dioxide and steam (57) in work in which the monotonic effect of increasing gas velocity was used to estimate the absolute reaction rate by increasing the gas flow until no further increase in reaction rate, as measured by gas analysis, was found."

The dependence of reaction rates on gas velocity could not be accounted for by a pure diffusion process. This led to the application of the concept of the stagnant film (55,58) to account for this effect. This concept has been an important part of the development of our understanding of general heterogeneous reaction kinetics.

As discussed subsequently the extensive application of the combustion of pulverized coal in large steam boilers occurred in this period. This led to the initiation of studies of burning particles in the size range of pulverized coal.

Tests with 60 to 90-mesh particles dropped through a heated tube showed that some coal particles ignited at about 1100°F but a temperature of about 1300°F was required to ignite the major fraction of the particles (59). Later tests (60) showed that a temperature of about 1500°F was required to obtain uniform ignition of certain bituminous coals.

Combustion of individual particles of coal is complicated by the formation of cenospheres (59) as a result of simultaneous softening and evolution of volatile matter which when burned shows up as a luminous gas flame in photographic studies (59). A theoretical analysis (61) indicated that for a given quantity of excess air the burning time of a solid particle is greater than that of a cenosphere containing the same weight of combustible. The magnitude of the difference depends on the ratio of the size of the cenosphere to the size of the original particle. Burning times increase as the quantity of excess air decreases.

After reviewing basic and applied work on the combustion of pulverized coal Orning (61) concluded "Considering all the data on the mechanism and rate of combustion, it appears that a transition must occur from diffusion to surface reactivity as the controlling factor. Immediately after the zone of ignition and burning of volatile matter, the particle temperature rises very rapidly. In this region the smaller particles burn to a low carbon content within a time proportional to the square of the radius of an equivalent solid sphere and to a function depending upon the influence of coal characteristics and flame conditions upon cenosphere formation.

The larger particles will still contain a considerable portion of the total carbon after the rate of heat release has passed its peak. Continued rapid combustion of these particles depends upon their ability to maintain themselves above a certain temperature. With the combustion rate, and hence the heat release, varying as the particle diameter while the rate of loss by radiation is proportional to the surface, the largest particles will have the lowest temperature.

The reactivity of the original fuel is no indication of the temperature at which the surface reaction begins to control. The high particle temperatures in the early stages of combustion transform the residue into a material whose reactivity is mainly a function of flame conditions. The characteristics of the original fuel appear in their effect on cenosphere formation, in a possible catalysis by ash, and in a hindrance by ash incrustations.

A complete calculation of burning times must consider the possibility that the surface reaction rate will begin to control beyond a certain degree of combustion. Lack of data on the reactivity and configuration of combustion residues and the dependence of particle temperature upon an equilibrium with furnace surroundings make it inadvisable to attempt a general solution."

Combustion in Fuel Beds

Combustion in fuel beds has been reviewed by Mayers (56), Nicholls and Barkley (49), and Haslam and Russell (3). This type of combustion encompasses the open grate, the central house-heating furnace and the various types of mechanical stokers.

At the beginning of our period extensive research had already been done to improve the convenience and efficiency of the coal fire-place (62). Also extensive tests had been made by the Bureau of Mines and others (63-66) on the combustion of various coals on a grate in a cylindrical furnace. These tests provided information on the effect of rate of firing on gas composition in the fuel bed and on the temperature of the fuel bed. The tests showed conclusively that the quantity of coal burned or the capacity of

the furnace depends entirely on the quantity of primary air coming into the furnace under the grate. The Bureau of Mines also studied the combustion of gases over the fuel bed and in this instance demonstrated conclusively that the quantity, distribution and turbulence of secondary air determines the efficiency of the furnace. Thus at the beginning of the period there existed a significant body of practical knowledge on combustion in fuel beds.

During the period additional work was done on the combustion of various coals in house heating boilers, (67) on the performance of domestic anthracite stokers, (68) on the fundamentals of combustion in small underfeed stokers (69) and on burning various coals in domestic overfeed stokers (70).

Most of the work on various types of stokers during the period involved improvements in mechanical design to secure a high degree of reliability and a high conversion of fuel into heat (71-75).

Mayers (56) states that "The conditions within the beds of travelling grate stokers have been determined experimentally (76-78). These investigations show that the layer of coal entering the furnace is ignited at the top of the bed; and that the surface dividing ignited from raw coal moves down as the layer passes through the furnace. The ignition surface reaches the grate ... where the dense flame of volatile matter stops; all the fuel has been ignited and coked at this point, and only the coked residue is burned out beyond it. As this process proceeds, a larger and larger proportion of the bed becomes ashy refuse. The fire should be operated so that all the fuel is burned out of the refuse short of the end of the grate, but the air quantity passing through this end of the grate must be controlled to prevent excessive losses."

Spreader stokers were a relatively new development in this period. The principles of operation are essentially similar, so far as the fuel bed is concerned, to those obtaining in hand-firing, the stoker being merely a means of producing a continuous flow of small amounts of fresh fuel down into it. Description of such units and the results of tests made on them are given by Barkley (79-80).

Combustion of Pulverized Coal

The use of pulverized coal in the firing of large steam boilers came into being at the beginning of our period. For example, the boiler heating surface fired with pulverized coal increased from 200,000 sq. ft. in 1918 to 2,000,000 sq. ft. in 1925 (44). The progress of this development throughout our period has been detailed by Orning (45), Haslam and Russell (46), and Nicholls and Barkley (49).

The early developments in pulverized coal combustion as well as developments later in our period have been summarized by Nicholls and Barkley (49) as follows:

"In 1917 a report (65) of the Bureau of Mines showed that a long travel of flame was required to give complete combustion unless the air and the combustible were mixed vigorously. When furnaces for pulverized-coal firing were so built they gave satisfactory performance and good efficiencies (81). The cooperative work of the Bureau of Mines and the Milwaukee Electric Railway and Light Co., resulted in the first successful application of pulverized fuel in the steamboiler field.

In the earlier designs successful removal of the ash required that the particles be deposited in a dry or unmolten state. These dry-bottom furnaces were not so successful with coals having low-fusion ashes. The problem was solved by going to the other extreme of maintaining the ash in a liquid state and tapping it intermittently or continuously; the wet-bottom furnace was the outcome.

Operation of these furnaces depends largely on the properties of the coal ash and its slag. As relatively few data were available, the Bureau of Mines initiated in 1929 a study on the ash factor in such furnaces and the properties of coal-ash slags in general (82)."

The initiation of the systematic study of coal-ash slags followed closely the first successful application of the slagging-type furnace (83) and the first studies on slagging conditions in full-scale furnaces (84). Other studies of conditions of temperature and gas compositions in full-scale furnaces were directed toward the explanation of the striking difference in refractory service conditions in two similar furnaces (85) and toward the effect of different burner and heat absorption configurations (86).

HYDROGENATION

Coal hydrogenation was practiced for the first time on a large scale in Germany in 1925 and subsequently in France, Great Britain, Japan and the United States (87). In commenting on these early developments Storch (88) states:

"Except for a relatively small amount of research published by the British Fuel Research Laboratory, little information on the fundamentals of coal hydrogenation is available, despite the voluminous patent literature, which is often more confusing than informative. Unquestionably much more is known by industrial interests, particularly in Germany and Great Britain, than appears in print. However, a study of the development of coal hydrogenation in these countries reveals that the intensive drive made during the past decade to achieve large-scale production has left little, if any, time and funds for fundamental research."

The literature on coal hydrogenation prior to 1931 was reviewed by Skinner and Zerbe (89,90) and between 1931 and 1938 by Fieldner (91). These reviews along with two books by Berthelot and Hot (92) and reviews by Storch (88) and Wu and Storch (87) cover the basic work on coal and tar hydrogenation in our period.

Studies of the hydrogenation of a number of British coals in small bombs showed that the yield of oil boiling below 360°C at atmospheric pressure increased approximately linearly with the carbon content of the coal. (93) As a corollary the reactivity of the coals to hydrogenation was approximately inversely proportional to their carbon content.

Similar studies on the hydrogenation of the mechanically separable constituents of American coals showed that the translucent constituents (spores, resins, oil algae, translucent attritus, and anthraxylon) are liquefied completely. The opaque constituents (fusain and opaque attritus) contain about 75 to 95 percent and 20 to 60 percent, respectively, of materials resistant to hydrogenation.

On the basis of the foregoing results, it was suggested (94-96) that "petrographic analysis would be a desirable, although only semiquantitative, tool for predicting liquefaction yield upon hydrogenation." This was confirmed by work done in the Bureau of Mines' experimental plant (97) which showed fair agreement between petrographic estimates of organic residue yield and yields obtained in the continuous operation of the plant. These tests were made on nine coals ranging in rank from lignite to bituminous A.

Laboratory work on the effect hydrogenating coal in the presence of a catalyst (stannous oxide), with and without a vehicle, showed that these two variables are not independent of each other (98,99). For example with small amounts of catalyst (less

than 0.1% of charge) the addition of a vehicle results in an appreciably greater yield of volatile products. With higher concentrations (more than 0.5%) the effect is small and may even become negative.

The extensive work done in our period on the effect of catalysts on the liquid phase hydrogenation of coal has been reviewed in considerable detail by Storch (88).

In laboratory studies, the catalytic effect of the walls of the converter cannot be neglected. (100) This effect is less important in large diameter industrial reactors although it may be of considerable importance in engineering development work involving the use of small diameter tubes (101-103).

The effect of the halogens in enhancing the activity of stannous oxide, stannous hydroxide, ammonium molybdate and nickel sesquioxide as liquid phase hydrogenation catalysts was demonstrated by the British (104,105) and Japanese (106,107). Results obtained with various catalysts on the liquid-phase hydrogenation of coal are generally applicable to the liquid-phase hydrogenation of tar (108).

The preparation and performance of catalysts for the vapor-phase hydrogenation of low temperature tar and middle oil has been discussed by Storch. (88) Information on such catalysts as supported molybdenum oxide, pelleted molybdenum or tungsten disulfide as well as on many others is also presented.

Tests on the effect of pressure on the liquid-phase hydrogenation of coal showed little effect on the capacity of a small-scale plant in the range of 180 to 250 atmospheres. (109) However, Pier (110) stated: "The conversion of old coals or of asphalts of high molecular weight, which goes but slowly at 200 to 300 atmospheres, proceeds without difficulty and at a satisfactory rate for large-scale production at considerably higher pressures, e.g., 700 atmospheres or more."

An increase in temperature in the range of 420 to 460°C increases the yield of crude gasoline, middle oil and hydrocarbon gas and decreases the yield of heavy oil (oiling of 300°C) and solid organic residue. (111,112) The hydrogen absorbed also increases with increasing temperature. The effect of temperature and contact time are analogous in that higher temperatures are equivalent to a longer contact time (111).

Storch (88) points out that "coal is usually hydrogenated for the single purpose of producing hydrocarbon fuels. Consequently, there has been little incentive to study the characteristics of intermediate products such as the "middle" oil (boiling range 210 to 330°C) from liquid-phase coal hydrogenation. As a source of organic chemicals, however, this intermediate product is most interesting and merits examination. The middle oils from liquid-phase coal hydrogenation contain benzene, toluene, xylene, cyclohexane, methyleyclohexane, about 20 percent of tar acids (phenol, cresols, xylenols), and 2 to 5 percent of nitrogen bases." In addition "several patents mention the isolation of many polynuclear aromatic compounds of high molecular weight from coal-hydrogenation products. Sometimes the actual isolation is preceded by dehydrogenation. Products of this kind include pyrene, chrysene, retene, fluoranthene, carbazole, methyl- and dimethylpyrenes, 1,12-benzoperylene, coronene, picene, fluorene, methylanthracene, and naphthalene." (88)

"The products of the hydrogenation of coal are largely aromatic and naphthenic in nature, whereas appreciable yields (about 12 percent) of the paraffin hydrocarbons have been reported in the hydrogenation of German brown coals (88)."

Tar may be hydrogenated under the same conditions as coal except that no solid materials other than a small quantity of catalyst powder in the case of high temperature tar must be introduced or removed from high-pressure vessels. Low-temperature

tar may be processed directly by mixing with recycle oil and hydrogen and passing the mixture over a fixed catalyst bed in a high-pressure vessel.

The effect of process variables on the yield and distribution of products are essentially the same as in the case of coal as shown in Storch's review (124) of tar hydrogenation covering our period. This review also shows that this similarity also exists in the nature of the products obtained from the two feedstocks.

SYNTHESIS OF HYDROCARBONS FROM MIXTURES OF CARBON MONOXIDE AND HYDROGEN

The catalytic conversion of mixtures of carbon monoxide and hydrogen to hydrocarbons which is referred to as the Fischer-Tropsch synthesis or the gas synthesis process was developed and commercialized in our period. The details of laboratory research and industrial development have been reviewed by Storch. (113) A more comprehensive treatise on the Fischer-Tropsch and related syntheses was published in 1951. (114) The vast amount of work done on the Fischer-Tropsch synthesis in Germany, Great Britain, Japan and the United States cannot be presented here. Instead, we will quote the excellent brief summary of developments in our period given in the book by Storch et al. (114)

"The Fischer-Tropsch synthesis had its origin in an observation made in 1923 by Franz Fischer and Hans Tropsch that alkalized iron turnings at 100-150 atm of hydrogen plus carbon monoxide and 400°-450°C catalyzed the production of "synthol." This product consisted chiefly of oxygenated compounds and a very small quantity of hydrocarbons. At 7 atm and, later, at 1 atm, Fischer found that the distribution of oxygenated and hydrocarbon products was reversed. The first Fischer-Tropsch catalyst was an iron-zinc oxide preparation which was reported by Fischer in 1925. It was tested at atmospheric pressure with a mixture containing 3 volumes of hydrogen and 1 volume of carbon monoxide, and at a temperature of 370°C. However, development of iron catalysts was unsuccessful until 1937, which was several years after the Fischer-Tropsch process was in commercial operation with a cobalt catalyst.

An important advance in the development of Fischer-Tropsch catalysts was the precipitation of nickel-thoria on kieselguhr in 1931. This catalyst was followed in 1932 by the corresponding cobalt catalyst, 100Co:18ThO₂:100 kieselguhr, parts by weight, which was the starting point in the development of the Ruhrchemie commercial catalyst. Subsequent changes in catalyst composition, concomitant with process development, resulted in a standard composition in 1937 of 100Co:18ThO₂:200 kieselguhr and in 1938 of 100Co:5ThO₂:8MgO:200 kieselguhr.

The advantages of iron over cobalt, in being easily available from many sources and in imparting flexibility to the process, stimulated continuous research on iron catalysts. In 1937, alkalized precipitated iron catalysts were successfully operated on a laboratory scale by the Kaiser Wilhelm Institut für Kohlenforschung at 15 atm of water gas and at temperatures of 235°-250°C.....

In the Fischer-Tropsch process as developed commercially by the Ruhrchemie A.G. in Germany in 1935-1940, synthesis gas containing 2 volumes of hydrogen per volume of carbon monoxide was compressed to about 7 atm and passed through a granular bed of cobalt catalyst at 185°-205°C. The major products of the synthesis were wax, oil, water, gaseous hydrocarbons, and a minor amount of carbon dioxide. The hydrocarbons were largely straight-chain paraffins. The olefin content varied with pressure, contact time, and temperature. Improved modifications of the Ruhrchemie process involved the recycling of exit gas from the reactor and the use of iron to replace cobalt in catalyst preparation. These changes increased the olefin content of the product and the flexibility of the process, particularly in the control of the proportions of gasoline, Diesel oil, and alcohols."

GASIFICATION

General

As in the case of combustion, research and development work on coal gasification in our period can be divided into basic studies and studies of and development of gasification processes. Work in the latter areas can be considered in three categories: (a) processes for making low-Btu or producer gas; (b) continuous processes for making intermediate heating value gas; and, (c) intermittent processes for making blue-water gas and carburetted water gas.

Basic Studies

In all gasification processes the endotherm of the steam-carbon reaction must be supplied by the combustion of some of the fuel with air or oxygen. Accordingly, the results of much of the basic work on combustion of carbon are also applicable to the gasification of carbon. However, gasification also involves the reaction of carbon dioxide with carbon and of steam with carbon.

Prior to our period considerable work had been done on the reaction of carbon dioxide with carbon to form carbon monoxide. This reaction is referred to as the "Boudouard reaction" (115) because Boudouard was the first to study its equilibrium. The reversal of the above reaction can occur in the gas space above the fuel bed and is referred to as the "Neumann reversal" (116) because Neumann was the first to direct attention to the possibility of its occurrence. The carbon dioxide-carbon reaction as well as the steam-carbon reaction were studied extensively by Clement and co-workers (117) and by Rhead and Wheeler (43,118). The former study presented data on the effect of temperature and time of contact on carbon dioxide or steam conversion. The latter study presented data on reaction rate constants and advanced the concept of a carbon surface covered with an adsorbed film of oxygen referred to as the "carbon-oxygen complex." During our period evidence was presented of the existence of the "carbon-oxygen complex" (46,119-121) and on its role in the mechanism of gasification reactions.

Basic studies of gasification prior to and during our period have been thoroughly reviewed by Mayers (56,122), Orning (61) and Haslam and Russell (3). In addition to reviewing such studies van der Hoeven (123) has reviewed developments in the production of producer gas and Morgan (124) has reviewed developments in the production of blue water gas. Work on the gasification reactions done prior to 1933 has been reviewed by Logan (125) and Elliott (126) who subsequently reviewed developments in the gasification field prior to 1940 (127).

As stated earlier (31) the reactivity of carbon to air, to oxygen, to steam and to carbon dioxide are all parallel. Therefore relative rates of reaction determined with one reactant are generally the same with one of the other of the above reactants.

Blakely and Cobb (128) studied the effect of contact time at two different temperatures on the rate of reaction of carbon dioxide with a variety of cokes and other forms of carbon and also the effect of temperature at constant time of contact. Reactivity decreased with an increase in contact time because the more reactive parts of the surfaces had already been consumed. Similar effects would be expected with steam.

In a study of the influence of coke reactivity on the formation of water gas Bunte and Giessen (35) observed that in the case of the more reactive cokes a large fraction of the steam was decomposed by the reaction forming one mole of carbon monoxide and one mole of hydrogen per mole of carbon. They pointed out that the value obtained for the quantity of steam decomposed was not characteristic of the actual conditions in

the fuel bed but was influenced by the subsequent establishment of water gas shift equilibrium in the gas phase.

P. Dolch (129) analyzed the data of Bunte and Giessen (35) and of M. Dolch (130) and concluded that there is no experimental evidence that the reaction of steam with carbon to form CO_2 and hydrogen occurs but that the reaction forming CO and hydrogen with the subsequent water gas shift reaction are of primary importance. In the experiments analyzed, water gas equilibrium was obtained at a temperature of 800°C with reactive carbon materials such as lignite coke and wood charcoal. With less reactive cokes, such as gas coke, water gas equilibrium was not attained until temperatures approached 1000°C .

In earlier studies of the steam carbon reaction (131,132) the catalytic effect of ash on the water gas reaction was observed. The first studies on the magnitude of the effect of catalyzing the steam carbon reaction were made by Taylor and Neville (133) in 1921 just prior to our period. They found that potassium and sodium carbonates were the most effective catalysts of all those investigated, and they clearly demonstrated that their effect was indeed catalytic. They believed that the catalysts accelerated the decomposition of the surface complex of carbon and oxygen suggested by Rhead and Wheeler (43), thereby exposing a clean carbon surface which was reactive to carbon dioxide. Carbon dioxide produced in the water gas shift reaction would then interact with this carbon to form additional carbon monoxide which in the presence of excess steam would react as above to form additional quantities of carbon dioxide and hydrogen, thus increasing the net increase of gas from the steam-carbon reaction.

Marson and Cobb (134) found that sodium carbonate was the most effective additive in gasifying laboratory coke at 1000°C . It was found that additions of potassium carbonate and sodium sulfate were just as effective in catalyzing the steam-carbon reaction as was sodium carbonate. In this same investigation it was observed that those additives which produced a maximum effect on the steam-carbon reaction exhibited an analogous effect on the reduction of carbon dioxide by carbon.

Additives were effective in the range of concentrations from 0.5 to 5.0 percent. Sutcliffe and Cobb (135) studied the effect of temperature on coke containing %5 additives of various constituents. The accelerated effect was considerably greater at 600°C than at 1000°C . Similar studies were made by other investigators (136).

Studies of the mechanism of the catalysis of the carbon gasification reactions (136,137) showed that the acceleration is brought about by the alternate reduction and reformation of the alkali carbonate in the following manner: The sodium carbonate first reacts with carbon yielding carbon monoxide and sodium in a mol ratio 3:2. The sodium thus transported into the gaseous phase is at liberty to react with carbon dioxide with the subsequent formation of carbon monoxide and sodium oxide. The sodium oxide may then further react with carbon dioxide to form sodium carbonate which is deposited on the carbon surface and is therefore capable of further reaction.

The steam-carbon reaction may also be catalyzed when carbon is deposited on a refractory impregnated with a sodium containing salt (126).

Toward the end of our period Dent and co-workers (138) laid the foundation for the hydrogasification of coal in studies of the kinetics of methane formation in the reaction of cokes and coals with hydrogen at elevated temperatures and at pressures ranging from 1 to 100 atmospheres.

Producer Gas

Studies of the reactions occurring in the fuel bed of a gas producer have been made by several investigators (3,139). The zones designated (3) from top to bottom are: ash zone; oxidation zone; primary reduction in which the steam-carbon and carbon-dioxide-carbon reactions occur; the secondary reduction zone in which the water gas shift and carbon dioxide reduction reactions occur; distillation zone in which the volatile matter in the fuel is added to the gas; and finally the gas space in which a decrease in heating value may occur as a result of the so-called "Neumann reversal" of the Boudouard reaction.

The effect of steam in the air blast of a producer was well known prior to our period (140). Additional work was done in our period (141,142) and it was established that the efficiency of the producer reached a maximum between 0.3 and 0.4 lbs. of steam per lb. of coal. However this range may have to be exceeded in practice to avoid clinker formation.

Work on the performance of full-scale producers done during our period was summarized (3,123). The latter reference discusses a variety of theoretical, thermodynamic and stoichiometric analyses of the producer gas process.

Development work on the slagging gas producer was done prior to our period (123). Data from tests on these producers (123,143) made in our period and on some of their further developments and operating characteristics were described (144).

Continuous Production of Intermediate Heating Value Gas

The use of oxygen in the blast of a producer was advocated (145-147) just prior to the beginning of our period. Experimental work (148) done first at atmospheric pressure led eventually to the development of the Lurgi process which operated at 20 atmospheres. Data on the effect of pressure in increasing the heating value of gas from the Lurgi process was presented by Hubmann (149) and Danulat (150).

The Lurgi process was commercialized in 1936 and made possible the continuous production of gas having a heating value as high as 450 Btu per cu. ft.

The Winkler generator which used oxygen or oxygen-enriched air and steam to gasify lignite or semi coke was developed and used commercially in our period (150,151). In this process a fluidized bed was used for the first time in gasifying solid fuel.

Carbureted Water Gas

The production of carbureted water gas reached a peak in 1926 (124) when it represented about 60 percent of the total manufactured gas in the United States. To put this into perspective, the energy in this quantity of gas represents about 0.5 percent of the energy in the natural gas produced in 1973. Today (1974) carbureted water gas is not being produced in the United States. In view of this, developments in our period will be mentioned only briefly. These have been discussed (124,127) and include the application of automatic controls; the use of mechanical grates; the substitution of heavy oil for gas oil; the application of the back-run process; reforming of refinery and natural gas in water gas generators; and, the production of high-Btu gas that could be mixed with or even substituted for natural gas.

SUMMARY

In the period 1924-1940 we saw many developments in fuel science and technology that were innovative and of lasting importance. Methods for classifying coals and their petrographic constituents were developed. Tests for determining the properties of coals and cokes were in many instances standardized. In the United States a standard method for carbonizing coal was developing to determine yields of coke, gas and tar and to evaluate the utility of these products.

In the field of combustion we advanced our understanding of the basic combustion reactions and of combustion of coal in fuel beds as well as in pulverized form. This latter development is up to the present time the most widely applied advance of any in our period.

In the area of gasification we also advanced our understanding of basic gasification reactions. But most importantly we saw many innovations such as the use of oxygen; gasification at elevated pressures; the use of fluidized beds in gasification reactors; the direct gasification of coal and coke with hydrogen; and the improvement of slagging gasifiers.

The period 1924-1940 saw the development and commercialization of technology for producing liquid fuels directly from coal and indirectly by the catalytic conversion of carbon monoxide and hydrogen produced from coal. Commercial synthetic liquid fuel plants were important to Germany in World War II but such processes are not generally economical today. However modifications of this technology may be economic in the near future.

The advances in gasification and production of synthetic hydrocarbons have not as yet had a major impact on the field of energy conversion but they most certainly will in the future.

It is apparent that the period 1924-1940 was most productive in developing fuel science and technology that has given us energy conversion technology that has made possible the widespread use of coal and other fuels in the generation of electricity today. In the emerging era of producing synthetic gaseous and liquid hydrocarbons from fossil fuels we will certainly draw heavily on the advances in gasification and hydrogenation made in the 1924-1940 period. Let us hope that the next 50 years of research and development on fuel science and technology and on other sources of energy will be as productive of useful technology as the first part of the past 50-year period.

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FUEL CHEMISTRY 1940-1960

by

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I. INTRODUCTION

During the period 1940-1960, the study of fuel chemistry was subject to a serious perturbation that persisted for 6-8 years (1945-53), after which research in this field essentially resumed its previous pattern. Dr. Fieldner gave an excellent review of this field in his paper for the ACS Golden Anniversary.

Up to the end of World War II, those doing research in fuel chemistry were concerned to a large extent with coal. The ranking of various coals, the determination of its components, the study of the properties of these components and especially attempts to elucidate the structure of the coal substance were some of the major subjects covered. The elucidation of the coal structure was investigated by studying the products found when various coals or coal fractions were subjected to a fairly wide variety of chemical reagents or treatments.

Those concerned with the utilization of coal were looking primarily for ways to convert it to a smokeless fuel (or at least reduce smoke formation), for ways to determine its coking properties, for ways to use blends as a means of producing a better coke for metallurgical uses, and for ways to reduce the amount of premium medium-volatile coals used so as to use a greater proportion of the less expensive high-volatile coals. The behavior of various coals under the influence of heat and pressure were studied in the laboratory and in a number of experimental ovens. The gas, oil, tar, and pitch resulting from carbonizations were examined and processes were developed for separation of many important chemical products.

The bulk of the research on coal was carried out by a relatively small number of organizations, almost all falling into three classes: the U. S. Bureau of Mines, several of the Schools of Mineral Industry in various universities, and a number of State Geological Surveys or Bureaus of Mineral Industries. This research partook substantially of an academic nature - the research people were in search of knowledge primarily for its own sake, but always with the hope that this knowledge would prove useful in the future.

The large consumers of coke did their research on carbonization primarily in order to develop more efficient, economical processes or to produce a more desirable end product.

The above do not by any means cover the full range of interests of the Fuels Division, but an examination of past programs shows that these subjects were predominant.

Toward the end of World War II, with its shortages and rationing and the expectation of "taking up where we left off", serious concern regarding the country's petroleum futures emerged. It was this situation which gave rise to the perturbation.

To show briefly the situation, Figure 1 shows the U. S. oil proven reserves and production during the years 1935-1944. The reduced rate of discovery and the then fantastic increase in consumption led to serious concern about our oil futures and resulted in the passage of the Synthetic Liquid Fuels Act. For a few years the interests of the Division of Fuel Chemistry were sharply focussed on the problems of producing gasoline from coal and from oil shale.

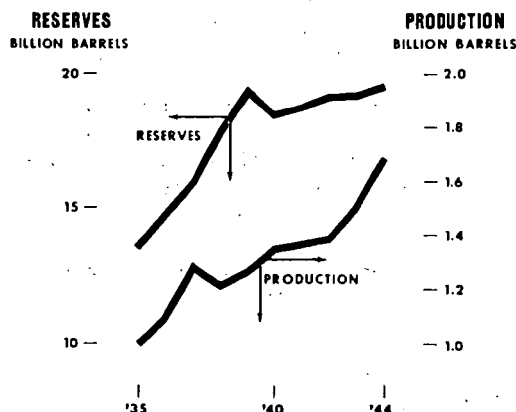


FIGURE 1. CRUDE PRODUCTION AND RESERVES, 1935-1944

Looking back over the programs of the Division meetings, between 1940 and 1960 we find a sharp rise (in many cases from none at all) in papers on coal hydrogenation, coal gasification, coal reactions, and Fischer-Tropsch synthesis. The emphasis was all on liquid fuels; no one thought of natural gas, except as a potential source of hydrogen for coal hydrogenation.

Institutions previously engaged in coal research promptly shifted the emphasis in their work toward the solution of what was generally regarded

as a most pressing problem. In addition, there began to appear papers whose authors worked for companies whose future was tied closely to petroleum or to products made therefrom.

The emphasis in research again shifted with the later advent of the Middle East oil at prices that were extremely attractive, and with the estimated reserves in the Middle East that seemed almost unlimited. Interest in liquid fuels from coal subsided very rapidly, the Office of Synthetic Fuels was eliminated, and many of the academic research workers (or their successors) returned to the study of coal as a substance - looking for an increase in knowledge that would contribute in the future to the advancement of science.

Rarely, if ever, has such a severe dislocation in a field of research been experienced, and rarely has interest in a particular area of science and technology disappeared so rapidly.

This is the period that we will attempt to explore. We will concentrate to some extent on the production of liquid fuels from coal, partly because it caused the perturbation and partly because of its present interest.

In order to supply some background we will review the fuels situation worldwide and in the U. S. during the period 1940-1960.

Because of its importance at the time and because of its relevance today we devote a fair amount of time to the production of synthetic liquids from coal, and the production of synthesis gas and hydrogen, also from coal. From some years these occupied the attention of many of those concerned with coal chemistry.

The history of the demise of that effort and a brief summary of the situation in 1960 will complete our story.

II. REVIEW OF FUELS SITUATION - 1940-1960

In the United States in 1940, there was little reason for concern regarding domestic energy sources. Coal, petroleum, and natural gas (locally) were all in abundant supply. Reserves, if considered at all, were judged to be ample for the foreseeable future. As a matter of fact, one concern was the persistent displacement of coal as a source of energy by petroleum and its derivatives and the consequent reduction of coal mining. Much natural gas was being flared or used for the production of carbon black, and the by-products were wasted to the air.

The distribution of our various sources of energy is shown in Figure 2 from 1940 to 1960. At the beginning of the period, coal supplied about half of our needs, but lost ground steadily; first to petroleum then after the advent of gas pipelines, to natural gas. By 1960 coal was supplying only about one-fourth of our energy needs. These needs had increased significantly during the postwar years. Petroleum, whose situation was so disturbing during the immediate postwar years had increased its share of the total energy consumption to about 42 percent by virtue of almost doubled production during the 20 years.

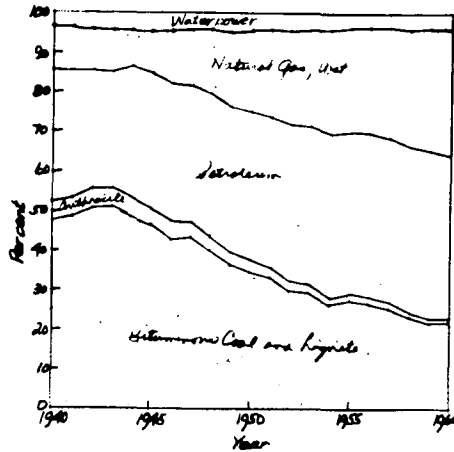


FIGURE 2. CONSUMPTION OF MINERAL FUELS AND WATER POWER IN U. S., 1940-1960

Natural gas, until the long gas pipelines were built, held quite steady at around 10 percent of the total. However, once there were means to distribute this gas, its convenience, cleanliness, and above all its low price led to remarkable gains. By 1960 gas was supplying almost one-third of our total energy consumption. Annual production rose from something under 4 trillion cubic feet in 1940 to 13 trillion cubic feet in 1960, a more than threefold increase. As we all know, this increase continued almost unabated for the next decade and led in large part to our present situation.

This then has been the pattern of the distribution of the energy load among our principal sources. It will perhaps be worthwhile to look at the situation for each one.

Figure 3 shows the story for coal production. No figure for reserves is shown because there are such wide variations depending on the basis for

the estimate. We have been assured by one of the power companies that we have more coal in the ground than the Arabs have oil. If this does not reassure us, then estimates ranging from 200 to 1000 years' supply should give some comfort.

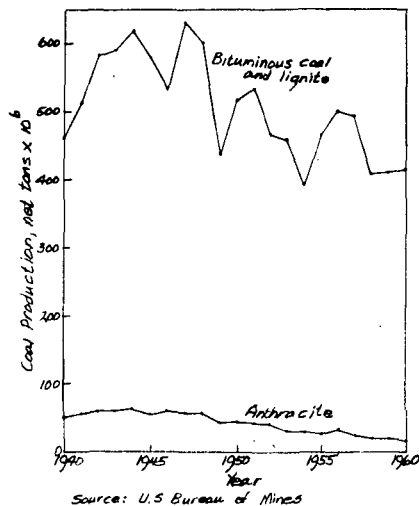


FIGURE 3. COAL PRODUCTION, 1940 TO 1960

The war and its aftermath gave some impetus to coal production, but the inroads of oil and gas began to show their effect and production of coal had decreased by almost one-third by 1960.

Figure 4 shows data on crude petroleum production. On this scale the sharp increase during the war is overshadowed by the continuing increase over the rest of the decade. World production, however, about 1950 began to show a tremendous rate of growth, doubling from 1950 to 1960. The U. S. share of world production dropped from over two-thirds to one-third.

Figure 5 shows the changes in world and U. S. reserves.

Known reserves in the U. S. showed a modest but steady growth throughout the period, but since production rose much more rapidly than new reserves, there was a significant decline in the reserves-to-production ratio.

The Middle East discoveries starting in 1950 began to grow at an almost unbelievable rate. From a little over 20 billion barrels in 1950, the estimated reserves rose to almost 200 billion barrels by 1960, a ten-fold increase in 10 years! After about 1957 reserves in other parts of the world began to increase also and the total world reserves rose to about 270 billion barrels.

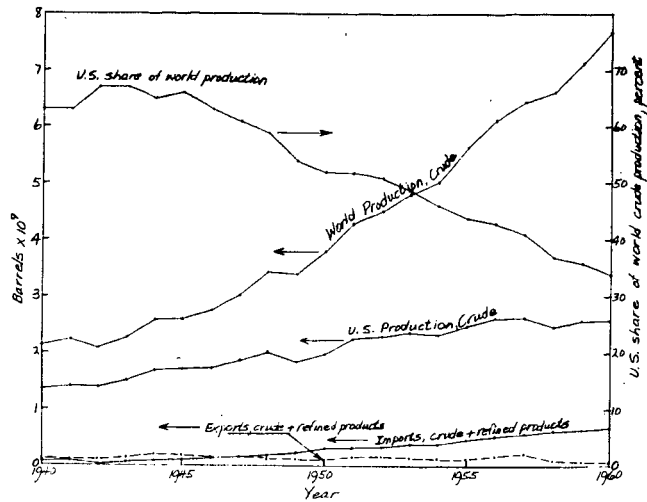


FIGURE 4. CRUDE PETROLEUM PRODUCTION

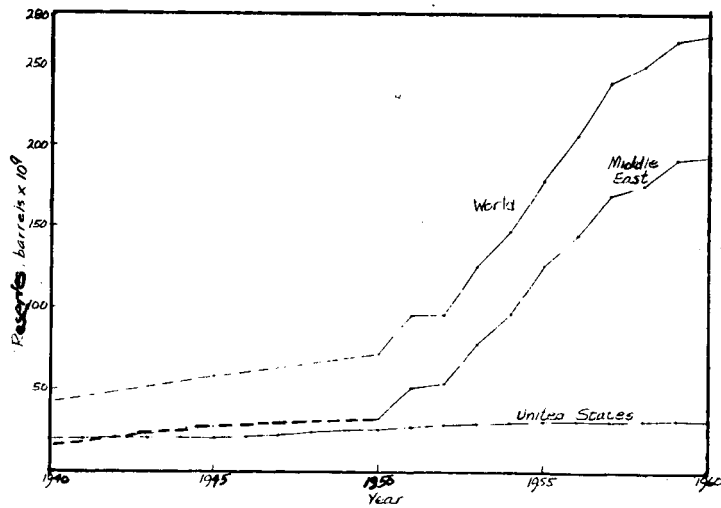


FIGURE 5. PETROLEUM RESERVES: FREE WORLD TOTAL, MIDDLE EAST, AND THE UNITED STATES, 1940 TO 1960

Figure 6 shows the history of gas during this period. In 1946 production was about 5 trillion cubic feet and by 1960 had risen to over 15 trillion cubic feet. However, for a number of reasons, the development of new reserves failed to keep pace with increases in production. In 1945 the ratio of reserves to annual production was over 30. By 1960 this had dropped to 20!

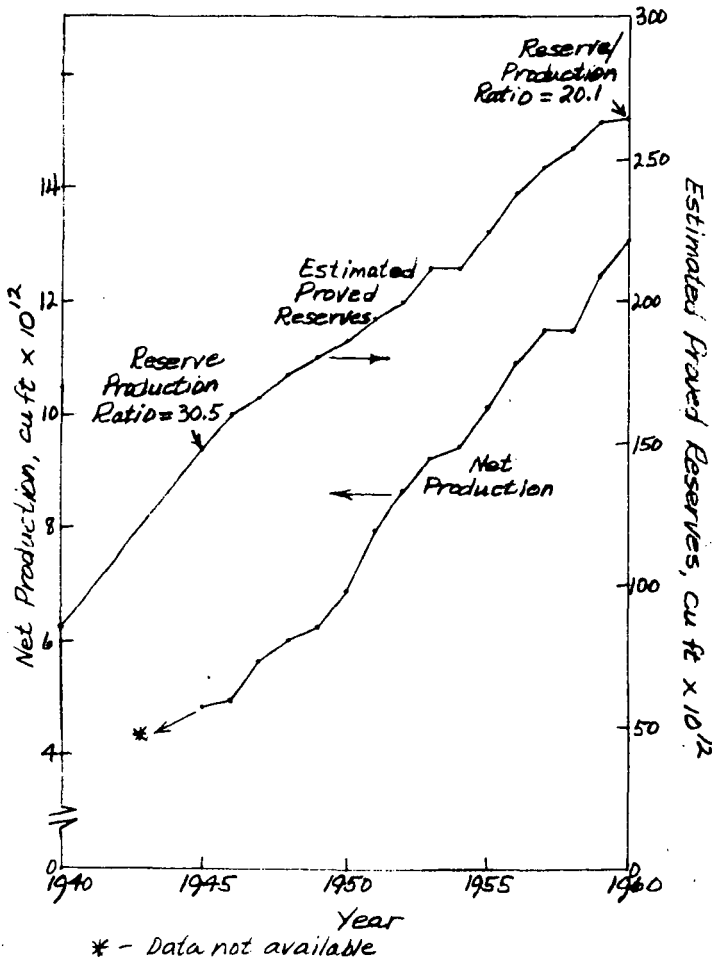


FIGURE 6. NATURAL GAS ESTIMATED PROVED RESERVES AND NET PRODUCTION, 1940 TO 1960

III. PRODUCTION OF LIQUID FUELS FROM COAL (1946-1953)

As noted above, the strong worry about postwar fuel supplies led to an almost complete dedication to solutions of the problems of producing synthetic fuel.

Not only was it necessary to develop coal hydrogenation processes, but also to develop the Fischer-Tropsch synthesis, the production of hydrogen and synthesis gas from coal, and finally the purification of those gases.

A. Coal Hydrogenation

In what seemed to be an emergency, the research and development work in the U. S. drew very heavily at the beginning on the information regarding German war-time activities. In the closing days of the war, British and U. S. Technical Oil Missions followed hard on the heels of the advancing armies, collecting documents, drawings, and intelligence concerning the top German men in the field who might be available for information and advice concerning the work in the U. S. and Great Britain. A considerable number of these men left Germany for England and the United States. Their contribution was significant.

German Practice. Germany used a variety of carbonaceous feedstocks in seven major plants. Detailed descriptions of these plants will not be attempted because of time limitations.

In general the coal was pulverized and made into a paste (50 percent coal) with a recycle heavy oil; catalyst was added and the paste preheated in the presence of some hydrogen as shown in Figure 7. The heated mixture passed through a series of three converters usually operating in the neighborhood of 900 F and 10,000 psi. By stepwise pressure letdown at the outlet, oil and gaseous product were separated and sent to the distillation system for recovery. The residue (ash, catalyst, unconverted coal, and the heaviest oil) was diluted with heavy oil, and centrifuged to recover as much oil as possible. The centrifuge residue was sent to coking kilns where additional oil was recovered and the solid residue was discarded.

The high-boiling portions of the product oil were vaporized and hydrogenated further over catalyst contained in a series of baskets in the vapor-phase converter as shown in Figure 8.* The character of the final products was determined by the amount of recycle and by the amount of hydrogen used. Any reasonable product mix was possible, but the lighter the product, the smaller the plant output and the greater the hydrogen consumption.

* At lower temperatures.

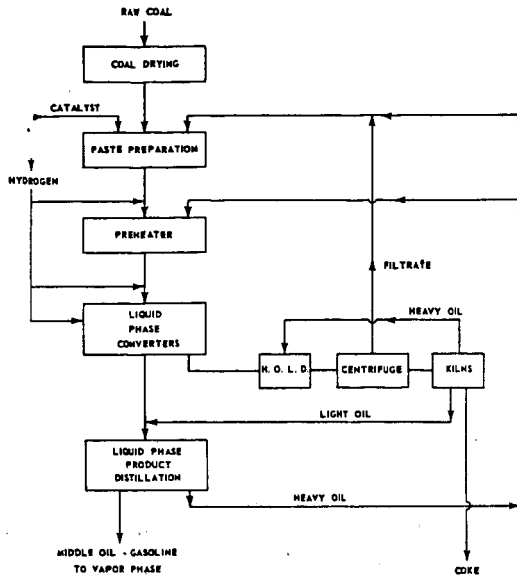


FIGURE 7. GENERAL SCHEME, LIQUID PHASE

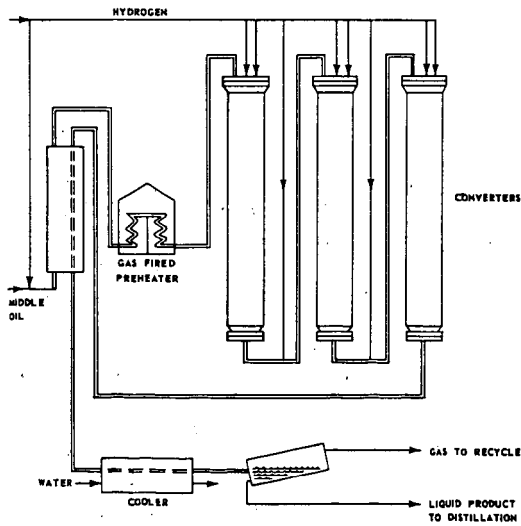


FIGURE 8. FLOW DIAGRAM, VAPOR PHASE

It should be borne in mind that although Germany produced over one-third of its total requirements by synthesis, this amounted to only 100,000 barrels per day. This may be compared with the 1973 consumption of 16-17 million barrels per day in the U. S.

U. S. Bureau of Mines Demonstration Plant. The construction of this plant was authorized by the Synthetic Liquid Fuels Act. The basis for the design was patterned after the German operations at Lutzkendorff and Welheim. The design was developed with the aim of applying modern U. S. engineering practices whenever such applications showed promise of increasing throughput or efficiency, promoting safety, or decreasing the cost of the gasoline product. The converters (2 liquid phase, one vapor phase) were 39 feet long and approximately 20 inches inside diameter. The plant was designed to charge just under 2 tons of coal per hour and to produce about 200 barrels per day. When the operations terminated in 1953, 2000 to 4000 tons each of four bituminous coals, one sub-bituminous coal, and one lignite had been processed.

The emphasis was on operability and, although, not all of the problems were successfully eliminated, a remarkable amount of progress had been made.

Bureau of Mines Pilot and Research Efforts. Research on coal hydrogenation started in the Bureau in 1936 and with the advent of the Synthetic Fuels Program a new laboratory was built at Bruceton, Pennsylvania. The bench-scale and pilot-plant research carried on here made a large contribution to the construction and operation of the demonstration plant. Studies were performed on new catalysts, catalyst preparation, effects of process variables, reaction mechanism, and other significant elements.

Activities in England. England had a commercial coal hydrogenation plant in operation in 1937. When war came, because of the bomb hazards, coal operations were terminated and the plant was used at lower pressures for the hydrogenation of creosote oils. Undoubtedly some research and development were carried on but references in the literature are scarce.

Union Carbide Company. The Union Carbide Company announced in 1952 the operation of its coal-hydrogenation plant at South Charleston, West Virginia. It was stated that the process would be aimed at the production of chemical raw materials and intermediates rather than liquid fuels from coal. Pressures were lower (6,000 psi maximum), temperatures lower, throughputs higher, and hydrogen consumption lower than in conventional liquid- and vapor-phase operations. A substantial part of the coal was liquefied to asphalt, and the announced intention was to feed this

to a unit for the production of metallurgical or specialty coke. The lighter products were to be processed to separate chemicals or classes of chemicals for sale or use as such. The unit was stated to have a design capacity of 300 tons of coal per day with the expectation that this could be increased as operating experience was gained.

Since operating conditions differed so widely from those actually required for gasoline production, this operation is not of direct interest in connection with synthetic fuels.

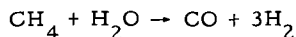
B. Fischer-Tropsch Synthesis

Work on the Fischer-Tropsch Synthesis had been carried out for many years in Germany and had been brought to commercial production, although on a limited scale.

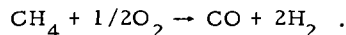
With the prospects of petroleum shortages in the U. S., interest in the process became widespread. In general, there were two basic approaches.

One was a high-temperature fluid bed synthesis aimed primarily at the production of gasoline. This was the path followed by the petroleum companies. Such a synthesis required a high ratio of hydrogen to carbon monoxide, to minimize deposition of carbon on the catalyst. In cases where cheap methane was available, the decomposition of methane with steam or oxygen was used as a source of synthesis gas.

The methane was reformed with steam:



or partial combustion with oxygen:



The hydrogen-to-carbon monoxide ratio was adjusted by water-gas shift if necessary to give the desired feed to the synthesis unit.

Construction of two commercial plants was started and one of these was put in operation. Little was published on the results except that the operation was not economically competitive at that time with gasoline from petroleum.

The second approach to liquid fuels from coal by the Fischer-Tropsch reaction was generally a compromise between the German operations and those contemplated by the oil companies. The coal was to be gasified as described below, the deleterious sulfur compounds removed, and the H_2 to CO ratio adjusted by the water-gas shift reaction, to produce the desired

feed to the synthesis unit. There were a goodly number of variations proposed each with its own advocates. Also, there was required a substantial study of the theoretical aspects of the process. The thermodynamics and kinetics of the various schemes were explored, and the work required was multiplied by the possibility of hot and cold gas recycle, additions of carbon dioxide or water to the feed, and a wide variety of means to remove the heat of reaction and to control temperatures. The search for new and improved catalysts also was pursued vigorously.

Undoubtedly much of the research and development related to the Fischer-Tropsch processes has never been reported, but the publications that did issue bear ample evidence of the large amounts of work that was done.

The Bureau of Mines Laboratories at Bruceton did much bench-scale and pilot-plant experimentation, and a demonstration plant was constructed and operated at Louisiana, Missouri. There still remained unsolved problems when the plant was shut down in 1953, but it is reasonable to believe that a reliable, sustained operation of this process could be achieved.

C. Coal Gasification

Whether coal hydrogenation or Fischer-Tropsch were used to make liquid fuels, hydrogen or synthesis gas would be needed in great quantities.

Petroleum consumption in the United States was in 1946 about 5 million barrels a day; if synthetic fuels were to make a significant contribution, outputs of 1/2 million barrels a day certainly could be visualized. Coal hydrogenation required about 8,000 cubic feet of hydrogen per barrel of liquid product, and the Fischer-Tropsch process required around 30,000 cubic feet of synthesis gas per barrel. Gas requirements then could range from 4 to 15 billion cubic feet per day, or 1.5 to 5 trillion cubic feet per year. On a volume basis, that is of the same order as the total natural gas production of the United States at that time.

Although it was proposed in some cases to make hydrogen or synthesis gas by reaction of methane with steam or oxygen, even in those days it was practical only if for some special reason methane was extremely low in price.

For most of the country, the source of synthesis gas or hydrogen must be coal, and the gasification of coal became the subject of very extensive investigation. If synthetic fuels were to be used widely, they must be produced in almost every part of the country and, if possible they must use coals locally available. This meant that the preferred gasification step should be one in which almost any coal was suitable. As is known today, this puts some very stringent restrictions on the gasification process.

Lignite seemed favorable because of its suspected higher reactivity, but the higher moisture and ash content, and the location of most of the lignite deposits did not make it attractive as the universal feed.

Much of the bituminous coal available in the heavily industrialized regions of the country was moderately or strongly caking, which difficulty would have to be overcome. In any case most of the coal-gasification process development work was aimed at a process that could use any coal as a feed.

Some processes operated at atmospheric pressure, but most were designed for operation at pressures that would permit gas purification and Fischer-Tropsch operations without further compression. For coal hydrogenation, compression costs would be substantially reduced with hydrogen at 300-400 psi instead of at atmospheric pressure.

Substantially all of the processes under investigation used oxygen and steam to gasify the coal. In the few attempts that were made to eliminate or minimize the use of oxygen, analyses showed that the economics were not favorable.

The surge of interest in this field can be illustrated by the United States patents granted on gasification processes. The following tabulation shows the number of patents granted whose application dates fall in the period indicated.

	<u>Number</u>
1930-1944 (avg/yr = 5.5)	77
1945	13
1946	25
1947	29
1948	28
1949	31

These figures apply only to United States patents.

It is not possible to discuss each of these many approaches. There are many literature references that describe them in detail and judging by the publications, many of the members of the Fuel Division at that time were heavily preoccupied with the problems of coal gasification. Except for the Bureau of Mines Synthetic Fuels Plant, and the Du Pont Company at Belle, West Virginia, most did not progress beyond a throughput of 100 to 500 pounds of coal per hour.

At Louisiana, Missouri, the Bureau was able to obtain a Linde-Franke oxygen plant with a production of 25 tons per day and the gasification section was designed on that basis. Coal was pulverized to about 80 percent through 200 mesh and transported by the oxygen to a Koppers-Totsek gasifier. Steam was preheated to about 2000 F in a pebble heater fired by natural gas.

The unit was a horizontal cylinder with steam, coal, and oxygen fed at each end and a gas offtake near the top center. After a waste heat boiler, the product was water scrubbed, passed through an electrostatic precipitator, and sent to the compressor or to atmospheric pressure storage.

The 2000 F steam superheat was to promote reaction and to reduce the oxygen demand. It was found that this was not economical and later operations in another unit used steam at 1000 F. The operation of these units was primarily experimental, and almost all of the gas supplied to the Fischer-Tropsch unit was made from coke in a Kerpely producer with steam-oxygen blast. (Operation of this process had been practiced for some years for the production of ammonia synthesis gas.)

The Du Pont Company installed a commercial-sized atmospheric coal-gasification unit in the plant at Belle, West Virginia, primarily for the production of hydrogen for ammonia synthesis. The design used was an outgrowth of their own development work, plus that of the Babcock and Wilcox Company in cooperation with the Bureau of Mines at Morgantown, West Virginia. The unit was designed for the production of 25 million cubic feet per day and is reported to have operated satisfactorily. No data have been published. After more than 2 years of use, operations were terminated in favor of the use of natural gas as a raw material.

Theoretical Studies. At the same time that the process development work was in progress, there was a large amount of research and development devoted to the thermodynamics and the kinetics of steam-coal-oxygen-synthesis gas systems. This work was essential to the design of the various gasifiers, it led to new gasifier concepts, and it led to means of increasing coal conversion and decreasing oxygen requirements.

D. Synthesis Gas Purification

The Fischer-Tropsch catalysts under investigation were in general very sensitive to sulfur poisoning, and much effort was devoted to purification of the synthesis gas from coal. Many commercial processes existed, but it was felt that further work would result in more efficient and economical processes. Except for that at Louisiana, Missouri, none of these newer approaches were placed in operation on a significant scale, but from the standpoint of fuel chemistry research and development, a considerable effort was expended.

IV. ADVENT OF INCREASED FOREIGN OIL SUPPLIES

Even as the United States was engaged in a major effort to develop oil supplies for our anticipated demand, the development began of new oil reserves in the Middle East and in Africa.

In 1951, the U. S. had a consumption of a little over 2 billion barrels per year and proven reserves of only 25 million barrels. Even at this low figure, only the Middle East showed more reserves, at about 50 billion barrels. World reserves were only 103 billion barrels.

By the end of 1961, proven U. S. reserves had increased to about 38 billion barrels and consumption had risen to over 3-1/2 billion barrels per year. Elsewhere, however, the situation was vastly different. The Middle East reserves had increased to almost 200 billion barrels, Russia's proven reserves were about equivalent to those of the U. S. Africa was beginning to be developed, as were other eastern hemisphere sources. New additions to reserves were being made in Canada, and in the Caribbean countries. World reserves had risen to 305 billion barrels in the face of rising consumption in the U. S. and in the rest of the world.

The increase in world reserves cast increasing doubt on the wisdom of continuing the urgent U. S. effort to develop synthetic liquid fuels. A change of administration in the U. S. added impetus to the movement to abandon this effort, and the Office of Synthetic Liquid Fuels was eliminated in 1953. The Demonstration Plants were shut down, laboratory staffs were reduced, and the research emphasis for those remaining was shifted to other lines of endeavor.

The programs of the Fuel Chemistry Division for the remainder of the decade reflected this change very quickly. Papers describing work on synthetic fuels almost disappeared, and other subjects began to replace them.

V. SITUATION IN 1960

At the end of 1960 then, we find the research in fuels chemistry focussed on much the same fields as in 1940. The upset occasioned by the effort on synthetic fuels had largely subsided and pressures associated with it had largely been relieved.

There were evidences of increasing concern regarding our diminishing domestic resources, especially with respect to natural gas. Some efforts

were being restarted on the gasification of coal and on the synthesis of pipeline-quality gas - but these were not extensive. Discussing this aspect further would probably carry this paper over into the realm of the following one.

Although the fields of fuels research generally were comparable to those in 1940, it does not mean that no progress was made during the 20 years. In spite of the war interruption, much fruitful work was done and our knowledge of the constitution, character, and utilization of fossil fuels had been advanced significantly.

ACKNOWLEDGEMENT

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ADVANCES IN FUEL CHEMISTRY 1961-74

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I. OUR CHANGING FUEL SUPPLY/USE PATTERNS

The 1961-74 period has been characterized as one of greatly expanding energy use, an increase of over 65% occurring in the United States in this period. (Table 1 and Fig. 1) (1). However, more fundamentally, it has been a period of change, a reversal from abundant, cheap fuels to one of real and impending fuel shortage.

The character of the fuel use pattern has altered significantly, with growth greatest in use of fuels for transportation and for generation of electricity. A new factor of far reaching importance has been fuel use restrictions imposed for prevention of environmental degradation. These restraints have affected the fuel use pattern, for example, in switching from coal to oil for generation of electricity.

There has also been a change in the fossil fuel supply pattern. Gas now supplies 33%, petroleum 43% and coal 19% of our energy needs. A new national feature has been the recognition that coal and oil shale must become major suppliers of energy in the United States in the period 1985-2000 and beyond. A significant activity therefore has been the initiation of a greatly expanded effort in coal and oil shale research.

The 1961-74 period is also unusual in the initiation of tar sands exploitation and also of the use of nuclear energy for power use, the latter growing to about 2% of our energy spectrum.

The 1961-74 period has been characterized by the spectacular growth in petrochemicals, with many examples of innovative chemistry contributing to the success of new products and improved processes for chemicals, particularly in the plastics field.

The changing patterns of fuel use and fuel supply have interacted with fuel chemistry, in that new and improved chemical processes have satisfied a need or in other cases, provided a means or cause for changes. There have truly been a number of breakthroughs, mostly in petroleum chemistry, no doubt because of the much greater research effort in these areas. It can be confidently expected that synthetic fuels chemistry will provide breakthroughs in this area in the next few decades.

II. PETROLEUM CHEMISTRY

The greatly expanded use of petroleum has been reflected in an intensive search for new and improved refining process technology seeking to make better products and to provide higher efficiencies. Remarkable improvements have recently been achieved in several refining processes, despite their relative maturity (>25 years) and past research effort. Thus, means of obtaining greatly improved yields of desired products and suppression of unwanted products have been uncovered for catalytic cracking, reforming and hydrocracking. Improvements in hydrosulfurization, although perhaps not as spectacular, are important, especially in the ability to process heavy petroleum residua.

A. Hydrocarbon Chemistry. Advances in hydrocarbon chemistry were reviewed by Schmerling in 1972 as part of a comprehensive Petroleum Chemistry Symposium (2). He concluded that perhaps the most important advance in theoretical hydrocarbon chemistry during the past fifty years was the postulation that highly reactive intermediates were involved. Such intermediates can be free radicals, carbonium or carbanion ions or others such as carbenes. Catalytic surface complexes should also be included. Earlier work by Whitmore describing carbonium ions postulated an electron-deficient carbon atom, this deficiency inducing a migration giving rise to a rearranged product. More recently Olah (3) has suggested that two types of positive carbon ions exist: The classical trivalent ion and a pentacoordinated non-classical ion. The pentacoordinated ion is considered to consist of five atoms bound to a carbon atom by three single bonds and a two-electron three-center bond. Postulation of the pentacoordinated ion has many advantages in explanation of reaction mechanisms.

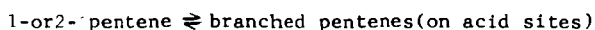
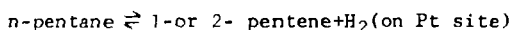
A very interesting catalytic reaction of olefins was described by Banks and Bailey in 1964 (4). They showed that alkenes undergo disproportionation to homologs of higher and lower molecular weight in the presence of alumina-supported molybdenum oxide, etc., at 100-200 degrees centigrade. Propylene, for example, was disproportionated to ethylene and n-butylenes at 94% efficiency at 43% conversion. The mechanism of the reaction may be considered to proceed by a four center ("quasicyclobutane") intermediate involving the four doubly-bonded carbon atoms of two molecules of olefin and catalyst.

Considerable progress has been made in alkali catalyst hydrocarbon reactions. The behavior of carban ions is remarkably different from that of carbonium ions. Alkyl groups in the former do not migrate. Primary carban ions are more stable than secondary ions which are more stable than tertiary. The reverse is true with carbonium ions. This leads to much different catalytic products.

B. Catalytic Reforming. Catalytic reforming of petroleum has taken great strides. The Free-World catalytic reforming capacity totals in excess of seven million barrels per day with about 50% of this capacity located within the United States and Canada. The bulk of the United States' capacity has been built during the last two decades in response to sharply increased demand, beginning about 1952, for high octane number gasolines needed to fuel high compression ratio, large-displacement engines.

Aromatics (benzene, toluene, and xylenes) are important components of the high octane reformate. The hydrogen produced as a "by-product" in reforming has become an increasingly valuable for use in associated hydrotreating and hydrocracking operations.

A significant advance was the recognition of the dual-function nature (isomerization and hydrogenation) of reforming catalysts (5). The mechanism of hydrocarbon reactions over such dual-function catalysts has been established and is illustrated for the isomerization of n-pentane (6).



Branched pentenes + $\text{H}_2 \rightleftharpoons$ isopentane (on Pt site). The amount of olefin present in the gas phase is extremely small because of the large excess of hydrogen used in the process and the moderate temperature and high pressure. It is important to recognize that dual-function catalysts can accomplish more than is achieved by passing reactants through two reactors in sequence, each filled with a different single-function catalyst (7).

As a result of mechanism studies and an understanding of the catalyst-hydrocarbon interaction, modifications of existing catalysts have been brought about. For example, improved selectivity has been achieved by changing the balance of functions.

Platinum-containing catalysts have dominated the field throughout the 1960's. Late in the 1960's several catalyst suppliers announced new catalysts which have come to be known as bimetallic. The early 1970's continued to show rapid development of additional bimetallic catalysts.

Bimetallic catalysts offer much higher activity and selectivity maintenance. The improved selectivity and activity permits operation at lower pressure and lower gas recycle ratios and/or higher severity.

The development of reforming catalysts capable of drastically improving performance represents potentially the most far-reaching improvement in catalytic reforming. These recent developments represent a "quantum jump" in catalyst performance (8).

The addition of rhenium to a platinum reforming catalyst results primarily in improving stability. Figure 2 shows data on Rheniforming a heavy naphtha at lower pressures (9). It has been suggested that some kind of platinum-rhenium couplet is involved, although it is now known

how this complex acts. Other metals and also sulfur are believed to have a beneficial effect. An important point is that platinum-rhenium do not per se lead to higher yields. However, higher yields can be achieved because such catalysts can operate at lower pressures where conventional reforming catalysts are not stable but at otherwise equivalent conditions, the initial yields are the same as those obtained with conventional catalysts.

C. Catalytic Cracking. A "quantum jump" improvement in catalytic cracking has also been achieved by the introduction of so-called crystalline aluminosilicate catalysts. The crystalline aluminosilicate, or zeolitic catalysts, are more active, more stable and produce considerably more of the desired products, gasoline and light fuel oil, compared to amorphous silica-alumina catalysts. They also produce considerably less undesirable products, coke and light gas.

The striking improvement in gasoline yield is evident from the following results (10).

Catalyst	Durabead(1) Amorphous	Durabead(5) Molecular Sieve
Yields Volume %, fresh feed		
Conversion	54.2	68.0
Heavy fuel	13.9	8.2
Light fuel	31.9	23.8
C ₅ +gasoline	39.9	53.1
Total C ₄ 's	13.3	14.7
Dry gas weight %	6.7	7.1
Coke weight %	3.5	4.8

Durabead 5, the first commercial zeolitic cracking catalyst was introduced in March 1962. Since that time a variety of other zeolitic catalysts have developed in both moving bed and fluid form. The zeolite catalysts now are used in over 90% of cracking units. The use of x and y zeolites with a pore size of about 10 Å has provided for even further improvements including very high activity. The ion exchanged faujasites can have cracking activities many orders of magnitude greater than silica-alumina (11). In turn, use of highly active catalysts have made possible process variations including riser cracking.

Crystalline zeolite are molecular sieves which have pores of uniform dimension of molecular size eg. 4 Å. Early concepts of molecular sieves as catalysts were to utilize them employing the concept of "shape selective" catalysts with pores which could accomodate molecules of certain molecular dimensions but exclude others, -eg. straight chain but not branched chain molecules. Actually, selective reactions were found possible (12), although later application for catalytic cracking using crystalline zeolites with pores in the 10 Å diameter have become the most significant application. While attention has been given to the unusual electronic charge fields in the pores of the zeolites to which reactant molecules are subject (13), much of the scientific basis of the catalytic action and selectivity of zeolites has not been resolved (14,15).

D. Hydrocracking. The decade of the 1960's witnessed the establishment of modern hydrocracking processes in petroleum refining. From a single demonstration unit of 1000 barrels per day capacity in 1960, commercial installations have grown to over 50 units with a capacity of about 800,000 barrels per day of total capacity. The demand for gasoline and middle distillates and the availability of low cost hydrogen have played major roles in their growth. The most significant factor has been the development of superior catalysts having excellent activity and activity maintenance at operating conditions far less severe than those used in the older hydrocracking processes.

Research is making available increasingly active and economical catalysts whose composition can be tailored to meet particular feed and product objectives.

The catalysts are dual-function catalysts having a critical balance. The chemistry of hydrocracking has been discussed and has been reviewed in terms of the balance of catalyst functions (16). (see also for references).

The "Paring" reaction is one of the most interesting new reactions discovered. As described (16), the products of hydrocracking hexamethylbenzene over a dual function catalyst are shown in Figure 3. The principle products are light isoparaffins and C_{10} and C_{11} methyl benzene. Essentially no ring cleavage occurs and hydrogenolysis to form methane is small. To account for the formation of isoparaffin products, a process of isomerization leading to side chain growth, followed by cracking of side chains of four or more hydrocarbons is proposed. The mechanism proposed is illustrated in Figure 4. Alkylcycloparaffins also exhibit the paring reaction.

E. Hydrodesulfurization. The desulfurization of petroleum is one of the most significant petroleum refining operations. With lighter petroleum fractions, desulfurization is important for subsequent catalytic refining steps eg. reforming. A new emphasis on the use of hydrodesulfurization particularly of heavy fuels has been imposed by the strict regulations for low sulfur content of boiler fuels, with an imposition of 0.8# SO_2 per million Btu (17) and even more strict regulations for some cities.

In 1960 there were about $2\frac{1}{2}$ million barrels per day of installed hydrotreating and hydrocracking capacity in the United States (about $\frac{1}{2}$ of oil processed). In 1971 this has grown to $5\frac{1}{2}$ million BPD or $\frac{1}{2}$ the 11 million BPD. Thus one of the remarkable features of hydrocracking is the rapid growth rate and high capacity reached. A second significant feature of commercial hydrotreating has been the application to heavier fractions including residua. The tag end of a heavy distillate with a 1050 degree F end-point may have a molecular weight of 800-900. Much of the sulfur in these cuts is present as substituted benzo and dibenzo thiophenes (18). Residua fractions contain asphaltenes present as highly dispersed colloidal material with an average molecular weight of roughly 5,000 to 10,000. To remove sulfur from such materials - more difficult because of molecular

structure - requires higher severity of hydrodesulfurization. This means raising the temperature, where other bonds will begin to break.

It is of interest to study the asphaltene molecule, where a structure shown in figure 5 has been postulated (19). The aromatic sheets are about 14 Å across and there are 4 or 5 sheets per stack. It is structures of this type which must be desulfurized.

The chemistry of hydrodesulfurization is only partially understood. Several excellent reviews have appeared (20, 21, 22, 23). Most researchers believe that for thiophene the reaction proceeds in two steps, the first producing butylene and hydrogen sulfide, and the second in which butylene is hydrogenated to butane. However, it is pointed out that the first step must be complex and proceeds through a butadiene intermediate. Much of the mechanism studies have been published by Beuther and co-workers.

Cobalt molybdate and nickel molybdate catalysts are used extensively. Relatively little is known how they act. In operation the active components exist as lower valence sulfides. Nickel-tungsten sulfides were used by the Germans. Diffusional effects are important.

The tolerance of catalysts to metals (N_1 and V from porphyrins) is important in maintaining catalyst life.

F. Other Petroleum Processes. Other developments have occurred in hydrocarbon alkylation, polymerization, isomerization and dehydrogenation. There have been many innovations in the chemistry of petrochemical manufacture. These are outside the scope of this review.

III. TAR SANDS

An historic event during the 1961-74 period was the initiation of commercial production of oil from the Canadian tar sands. This began in 1967 in a plant designed to produce 45,000 barrels per day. The Athabasca sands cover 12,000 square miles and contain 600 billion barrels of oil in place. The plant built by the Great Canadian Oil Sands Company is based on a four-stage sequence of mining, materials handling, extraction and heavy oil upgrading (24). Extraction is by a hot water system. The heavy oil is processed in delayed coke drums. The overhead is separated into three streams: naphtha, kerosene and heavy gas oil. These streams are hydrogenated individually and then blended to form a product called synthetic crude. While many unusual mining situations are encountered, the processing of the tar is by previously known petroleum refining techniques, although now applied to an unusual material. The separation of the tar from the sand by hot water processing has presented an important surface chemical field. A second 80,000 barrels per day plant has been proposed with several different process steps, many of them in the mining and conveying (25).

In clearing the primary oil, a thermal dehydration-cyclone arrangement will take the place of a dilution-centrifuge system.

In primary conversion, hydrovisbreaking will replace delayed coking. Again, the innovation is in the application of refining to the tar sands.

The chemical constitution of tar sands has been characterized further using modern analytical tools, including the nature of the sulfur compounds (26, 27).

IV. OIL SHALE

Oil Shale is an important potential source of fossil fuel in the United States in amount being second only to coal as a resource. The potential estimated from the Green River formation is between 600 (high grade over 25 gallons per ton of rock) and 1,800 (total) billion barrels of oil. Most of the oil shale is on federal lands. An unsuccessful attempt was made in 1968 to lease a few selected tracts. However, events so changed that a second program of leasing in 1973 of four tracts of about 5,000 acres each, has met with highly competitive bidding, the winning bids on the four tracts amounting to nearly \$500,000,000.

Over the years, most technical effort has concerned mining of the oil shale and various mechanical means of retorting it. Retorting of the oil shale has been carried on a fairly large experimental scale of about 1,000 tons per day, employing several different types of retorts (28). A demonstration plant began operation in Brazil using direct fired shale calcination. Burning of oil shale for power generation continued in Europe.

The chemical nature of shale oil has been further defined, as shown in the following table (29).

INSPECTION DATA ON TYPICAL SHALE OIL CRUDE

Gravity API	19.8
Pourpoint °F	83.5
N wt.%	2.1
S wt.%	0.7
O wt.%	1.7
C wt.%	83.9
H wt.%	11.4
Conradson Carbon	4.7
Bromine No.	33.2
Sediment wt.%	0.04
Ni ppm	6.4
V ppm	6.0
Flash °F	108.
Molecular wt.	328.

Investigations of the structure of kerogen are difficult because kerogen is a large complex molecule belonging to the multipolymer class, its insoluble nature and its inhomogeneity. Colorado oil shale of the Green River formation contains about 16% insoluble organic matter called "Kerogen." This represents about 4/5 of the organic matter present. The other 1/5 soluble organic matter represents "soluble bitumen." Using a combination of micro-pyrochromatography, separation and mass spectrometry, provided a structure for kerogen shown in figure 6 (30). X-ray diffraction has also been used for determination of the structure of kerogen (31).

In situ production of oil shale has shown promise. There are potential advantages both from avoidance of mining costs and a lessening of possible environmental damage. In situ tests at Rock Springs provided a crude shale oil which has been characterized and its conversion into an oil suitable for refining in a petroleum refinery demonstrated (32, 33). Recently, the press has reported tests for in situ shale oil production in which a cavern corresponding to a fraction eg. 25% of oil shale is removed, the oil shale above it fractured to form a permeable rubble, and the whole shaft then calcined to drive off the shale oil with improved economics.

The fracturing of the oil shale with chemical explosives has been described (34). It was shown that the explosion will propagate in water-filled natural fractures and sand propped, hydraulically induced fractures in oil shale. The shale was fragmented by this method and a successful underground retorting experiment to recover shale oil was performed.

The use of nuclear detonation has also been proposed. An interesting proposal is the bioleaching of oil shale and experiments have shown promise (35).

The hydrogasification of oil shale has been described. It was shown that the presence of hydrogen, even low pressure, significantly increases the organic carbon deposit compared with hydrogen-free retorting (36).

Studies on the chemical nature of kerogen showed the feasibility of using kerogen as a natural raw material for the synthesis of monomers, not by traditional pyrolytic methods, but by direct chemical processing resulting in the scission of native polymethylene chains, structural elements of the natural polymer, in the form of mono-acid and preferably dicarboxylic acids (37). Conventional industrial oxidants have been found to be suitable for direct oxidative destruction of the kerogen to saturated dicarboxylic acids. Kerogen treated with nitric acid and molecular oxygen yields 55% of $C_4 - C_{10}$ dicarboxylic acids.

In certain oil shale zones, the rock contains appreciable percentages of potentially valuable saline minerals. Trona ($Na_2CO_3 \cdot NaHCO_3$), associated with oil shale, occurs in vast quantities in Wyoming's Green River basin. In Colorado nahcolite ($NaHCO_3$) and dawsonite ($NaAlCO_3(OH)_2$) have been discovered in a zone 700 feet thick, also associated with oil shale.

Environmental protection and water usage continue to be of great concern in oil shale processing. Spent shale has been found to have properties similar to low quality cement, enhancing its disposal in compact fills. It can also be made to support vegetation. Disposal areas must be designed to prevent leaching of soluble minerals.

V. COAL

During the period 1961-74 scientific progress was made in further elucidating the structure of coal, using modern instrumentation, and in establishing the factors involved in chemical reactivity of coal. On the applied side, major efforts were made in developing chemical processes to remove sulfur dioxide from products of coal combustion (stack gas scrubbing). Over \$200 million has been spent in such installations in power plants in what must still be regarded as an experimental program.

A. Coal Gasification (38-42). For the most part, the gasification processes under development are closely related to the technology developed in the 1930's. In general the chemistry of high temperature gasification reactions remains the same for all processes. It is the mechanical and engineering variations which characterize the processes, particularly those features for supplying heat for the endothermic $C+H_2O$ reaction.

The required heat can be furnished by any of several methods: partial combustion of coal with oxygen, by electrical energy, by inert heat carrier, heat released by reacting CO_2 with metal oxide, or use of nuclear heat. Four large coal gasification pilot plants are in operation or are being constructed in the United States. Each involves fluid bed operation in contrast to the so-called fixed bed design of the Lurgi process which is in use in Europe. These four processes do involve certain novel chemical features. In the IGT Hygas process (hydrogasification), char formed in the process is reacted with steam using electrical energy as the heat source. The gas so formed, rich in H_2 and low in CO_2 is reacted with pretreated coal to produce a gas with high methane content. Since the hydrogen content of coal (averaging about 5 wt. %) is very low compared to that of methane (25%) coal gasification consists chemically of adding hydrogen to coal. In addition S, N and O constituents are converted to H_2S , NH_3 and H_2O respectively. The Hydrane process also converts coal to methane by hydrogasification.

Perhaps the most novel process in pilot plant stage is the CO_2 acceptor process. This process utilizes the reaction between hot lime (CaO) and CO_2 to furnish the required gasification heat. By use of a separate regeneration vessel, air is used instead of oxygen as in the Synthane or Bigas process.

One unique feature of the Synthane process is the use of a "tube-wall" reactor for methanation. The catalyst is a Raney nickel applied to heat exchange tubes by a flame spraying technique. This provides for highly effective heat transfer system. Another unusual methanation technique is provided by a liquid phase catalysis system.

The ideal gasification reaction for gasification of carbon is $C + 2H_2O \rightleftharpoons CH_4 + CO_2$, which is balanced chemically and nearly so calorimetrically. However, because the steam-carbon reaction does not proceed fast enough at lower temperatures, the reaction is carried out at 900 degrees C or above. Attempts have been made to operate at lower temperatures by catalysing the carbon-steam reaction, with partial success. One intriguing fact is the known capability of micro-organisms to convert cellulose to $CO_2 + CH_4$ at ambient temperature. While cellulose is somewhat different from coal, lignite can have an oxygen content of more than 20%.

The use of nuclear heat for coal gasification has been of considerable interest and is being actively investigated in Germany.

The in-situ gasification of coal is once again being tested experimentally in the United States since it offers many potential advantages.

There are other novel coal gasification processes in the research stage. The molten salt process and self-agglomerating process are further examples.

Interest has increased tremendously in coal gasification in recent years. The symposia reference (42), provide detailed information. Also, research needs have been critically analysed (43).

B. Coal Liquefaction. The conversion of coal to liquids can be carried out by four generic procedures.

1. pyrolysis to produce a gas, liquid and char
2. "solvent refining"--actually involving the transfer of hydrogen from a hydrogen "donor" organic molecule with some additional hydrogenation catalyzed by coal ash constituents
3. Fischer - Tropsch synthesis in which coal is converted to $CO + H_2$ which are then reacted to form hydrocarbon and alcohols
4. Direct catalytic hydrogenation

Several large pilot plants have been constructed recently in the United States to test new technology and several more are planned.

At the present time, the FMC Corp., under sponsorship of the Office of Coal Research, is operating a large COED (Coal Oil Energy Development) pilot plant with fluid bed pyrolysis (44). Powdered coal is subjected to increased temperatures in four successive fluid beds. Volatile liquid products are withdrawn at each stage and hence not subjected to the highest temperature where further cracking would occur. In this way maximum liquid yields are obtained.

Another type of process begins by treating coal with a hydrogen-donor solvent. There are several promising processes of this type under development in the United States (45). Broadly speaking, two categories are possible, those in which liquid extraction is carried out in a separate first step, and those in which extraction is carried out in the presence of a catalyst and under hydrogen pressure. The operation at Cresap by Consolidation Coal Company (44), and sponsored by OCR is of the first category; the hydrogen-donor solvent is hydrogenated in a separate step so as to regenerate its solvent capabilities.

Solvent refined coal. The dissolution of coal by organic agents under elevated pressure and temperature has long been known. German chemists Pott and Broche found a mixture of tetralin, phenol, and naphthalene to be the most satisfactory for bituminous coal. A key feature is that tetralin is a hydroaromatic "donor" able to transfer hydrogen to coal. This transfer is by a thermal, free-radical mechanism that is not accelerated by the pressure or hydrofining or cracking catalysts.

A pilot plant processing 6 tons of coal per day built by industry began operating in 1974 using a solvent refining process. The PAMCO solvent-refined coal process developed by Pittsburgh and Midway Coal Mining Company consists of mixing pulverized coal with a coal-derived solvent having a 500 degrees to 800 degrees F boiling range, passing the mixture with hydrogen through a preheater and reactor at about 1000 psi, separating the hydrogen plus hydrogen sulfide and light hydrocarbons formed, filtering the solution, flash evaporating the solvent and recovering the solidified coal product. The chemical analysis of charge and product is shown below. During the reaction phase, hydrogen reacts with part of the organic sulfur compounds forming the hydrogen sulfide. The hydrogen also stabilizes the solubilized coal products. The pyritic sulfur leaves the process in the filtration step, as does the other ash components.

	Kentucky No. 11 coal	Refined coal
Ash	6.9	0.1
C	71.3	89.2
H	5.3	5.0
N	0.9	1.3
S	3.3	1.0
O	12.3	4.4
Btu/lb	13,978	15,956
Melting point degrees C	----	128

Under the sponsorship of OCR a large pilot plant has been authorized for construction and operation in the State of Washington. This plant to start in 1974 will not only test scale-up factors, but will also produce sufficient product for larger scale testing of its combustion characteristics.

Scientists at the Bureau of Mines discovered that using a mixture of $(\text{CO}+\text{H}_2\text{O})$, or $(\text{CO}+\text{H}_2\text{O}+\text{H}_2)$ is even more effective than using H_2 alone for hydrogenation. The mechanism is related to the shift reaction $(\text{CO}+\text{H}_2\text{O} \rightleftharpoons \text{H}_2+\text{CO}_2)$ during which the hydrogen at an intermediate stage, possibly as the formate ion, is in a particularly reactive state. It should be possible to test the use of synthesis gas plus steam as an improvement in the solvent refined coal process.

H-coal process. The H-Coal process utilizes an ebullated bed reactor system developed by Hydrocarbon Research Inc. A unique feature of this reactor system is the ability to operate a catalyst system continuously with a feed consisting of solids, liquids, and gases. The upward flow of the feed maintains the catalysts in a state of rapid motion and permits the continuous passage of unconverted coal and ash from the reactor. Catalyst can be added and removed from the reactor during operation.

The production of low-sulfur fuel oil from coal by the H-Coal process has been discussed (47). It is stated that processing conditions can be varied to attain 1.5 to 1.0% S without ash removal, 0.5% S with ash removal and increased conversion severity, and 0.25% S with secondary treatment of part of the product.

For example, processing an Illinois No. 6 bituminous coal 3.6 bbls of C_4 + liquids were made/ton dry coal at 93% coal conversion. The sulfur content of the coal was 3.4% and of the liquids was 0.5%.

Turbulent catalytic reaction. In experiments conducted at the Bureau of Mines (48), a high-sulfur bituminous coal suspended in oil derived from coal was converted to a low-sulfur fuel oil by continuous processing through a fixed bed of pelletized cobalt molybdate alumina catalyst, under conditions of highly turbulent flow or hydrogen to prevent obstruction of the flow and to promote catalytic contact. From coal having 3.0% sulfur and 9.4% ash, the totally coal-derived centrifuged synthetic fuel oil, produced at 2000 psi and 850 degrees F had 0.31% sulfur and 1.3% ash. The data indicated that more selective separation of unconverted residual coal would provide fuel oils with sulfur content as low as 0.1% sulfur because the bulk of the sulfur is in the benaene-insoluble fraction of the product oil.

The new catalytic concepts for direct hydrogenation was previously reviewed (45, 49), references are detailed. A list of the systems is given below.

NEW HYDROGENATION CATALYTIC SYSTEMS

"Nascent"-active hydrogen generated in situ

Complexes of transition metals

Massive amounts of halide catalysts

Organic hydrogen donor solvents

Alkali metals

- (a) With H_2
- (b) With amines
- (c) Electrocatalytic

Reductive alkylation

Miscellaneous

Active hydrogen generated in situ. A combination of carbon monoxide and steam can hydrogenate coal more rapidly and to a greater degree than does hydrogen itself under the same conditions of temperature and pressure. The suggestion has been made that hydrogen, generated in situ by the water gas shift reaction between CO and H_2O , is in an activated form. It has also been suggested that the mechanism is via a formate ion.

Complexes of transition metals. Certainly one of the most, if not the most, significant development in the field of catalysis in recent years has been the discovery of a variety of new, and often unusual, catalytic reactions of transition metals and coordination complexes. The catalytic properties depend upon the central ion and the number and character of ligands. Some of these catalysts are soluble and have therefore been called homogeneous catalysts. Knowledge of their electronic structure has enabled the establishing of catalytic mechanisms on a molecular basis.

The capability of such metal-ligands complexes to react with hydrogen to form active species and the existence of coordinatively unsaturated metal complexes are fundamental to the mechanism of their reactivity.

One of the earliest and most important examples of their type of catalysts is cobalt carbonyl which, in the presence of $CO+H_2$, is capable of hydroformylating olefins. Cobalt carbonyl is also active in hydrogenating certain aromatic compounds and coal. Dicobalt octacarbonyl, in the presence of carbon monoxide and hydrogen, functions as a selective homogeneous hydrogenation catalyst for polynuclear aromatic hydrocarbons.

Coal was also treated with $CO+H_2$ in the presence of dicobalt octacarbonyl at the same temperature, 200 degrees C. Both H_2 and CO were added to coal under these conditions. Thus, this is one of the most active catalytic systems ever observed for coal hydrogenation.

Massive amounts of halide catalysts. The use of halide catalysts in amounts comparable to the coal or polynuclear hydrocarbons used has given some unusual hydrocracking results. Comparison of a $SnCl_2$ /coal ratio of 0.01 and 1.0 illustrates that while about 85% of the coal was converted to benzene solubles in each instance, the asphaltene conversion--the difficult step--was nearly completed with the larger amount of catalyst. Similarly, large amounts of zinc chloride were effective, and this compound was superior to conventional hydrocracking catalysts for coal or coal extract. Zinc chloride gave more rapid reaction, more complete conversion than conventional catalysts, and a very high octane without reforming.

Compared with conventional catalysts, molten zinc chloride more than doubled the conversion and hydrogen consumption when using a hydrocracking residue as feed stock, even though a lower temperature was used. Note-worthy also, is the high selectivity of the process for production of gaso-line and the high ration of isoparaffins to normal paraffins.

Hydrogen donor. The solution of coal by extraction using organic agents under pressure has long been known, and a vast literature exists. The German chemists, Pott and Brosche, found that a mixture of tetralin, phenol, and naphthalene was the most satisfactory solvent for bituminous coal. A key feature is the presence of tetralin which is a hydroaromatic "donor," able to transfer hydrogen to coal. This transfer is by a thermal, free-radical mechanism. The structure of the donor is important. The function of the phenol is apparently to assist in pulling the hydrogenated coal into solution. This combination effect is demonstrated in the table below where, it is seen, the synergistic effect can be built into a single molecule, o-cyclohexylphenol. The process mechanism is complicated. For example, much of the oxygen is eliminated in making the coal soluble.

LIQUEFACTION OF BITUMINOUS COAL BY HYDROGEN DONOR SOLVENT*

<u>Vehicle</u>	<u>% Liquefaction</u>
Naphthalene	25
Cresol	32
Tetralin	50
o-Cyclohexylphenol	82

* 0.5 Hr. at 400 degrees C.

Alkali metals. The alkali metals can act in hydrogenation of coal in several related ways: (a) as a direct hydrogenation catalyst (with molecular H_2), (b) with amines, and (c) in a catalytic electrochemical reduction.

Reductive alkylation. The formation of aromatic hydrocarbon anions is made possible by reaction with alkali metals. For example, naphthalene, dissolved in hexamethylphosphoramide, reacts with one or two moles of lithium to form the mono- or dianion. In turn, the dianion can react with CH_3I to give 9,10-dimethyl 9,10-dihydroanthracene. This is called reductive alkylation, since one of the aromatic nuclei is converted to an alkylated dihydrobenzene.

Reductive alkylation can also be carried out with coal substance. Although only 3% soluble in HMPA, coal became 90% soluble on addition of lithium to a suspension of coal in HMPA. Alkylation of coal with ethyl iodide-yielded an ethylated coal which was 35% soluble in benzene at room temperature. It was estimated that the alkylation corresponds to 1 alkyl to 5 carbon atoms. Reductive alkylation is also a means of adding hydrogen,

in that H/C of coal is increased. This alkylation method is much more effective in causing solubility of coal than addition of an equal number of hydrogen atoms. Moreover, a degree of benzene solubility is achieved which is not possible by hydrogenation.

The alkylation of coal was not restricted to use of HMPA. Coal can be readily alkylated in tetrahydrofuran, provided a small amount of naphthalene is added which acts as an electron-transfer agent.

Other novel hydrogenation systems. There are a number of other novel hydrogenation systems. These include volatile catalysts such as iodine, dehydrogenation of coal to form hydrogen (9000 ft³/ton) which possibly could be combined in a dehydrogenation-hydrogenation disproportionation process, use of molecular sieves containing metals to bring about hydrogenation of selected molecules, high-energy modification of coal or catalysts, use of ultrasonics to increase coal solubilization.

C. Combustion. Space does not permit the review of advances in the chemistry of combustion. Important new knowledge has been obtained which relates to combustion control for prevention of pollution. Thus it is possible to control combustion in a manner which minimizes NO_x formation, of particular importance in coal combustion. Likewise, the use of limestone addition in combustion for removal of SO₂ may become of major practical importance in developing fluid bed combustion. The chemical removal of SO₂ from stack gases is an alternative to synthetic fuels from coal in many large installations (50). The competition between synthetic fuels and stack gas scrubbing promises to become even more important and both processes are economically dependent on future advances in their respective technology (51).

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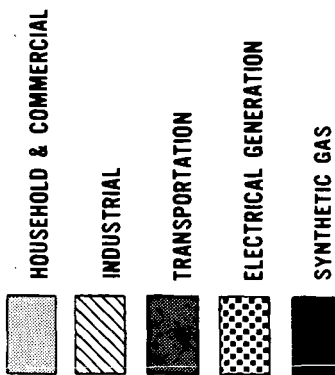
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UNITED STATES ENERGY CONSUMPTION BY SECTOR

1971 - 2000

(QUADRILLION BTU's)



USE SECTORS	1961	1971
Household & Commercial	10.4	14.3
Industrial	14.6	20.3
Transportation	11.0	17.0
Electrical Generation	8.5	17.4
Total	44.5	69.0

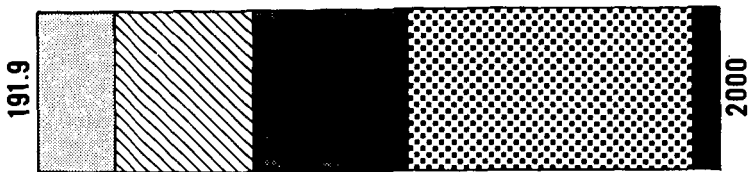
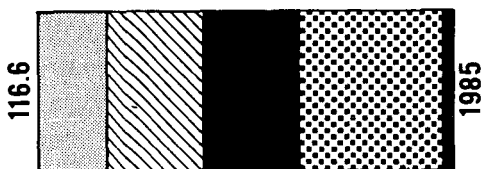
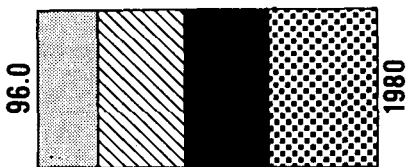
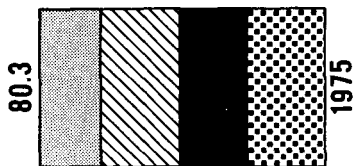
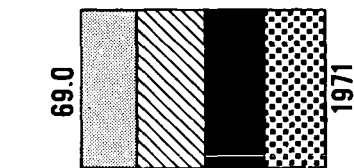
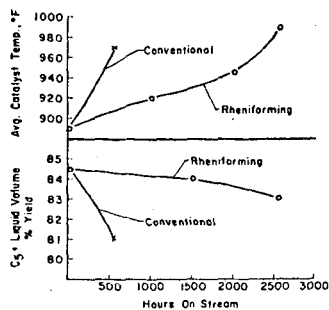


Fig. 1

Fig. 2



Rheniforming of 420°F Isomax naphtha.

Fig. 3

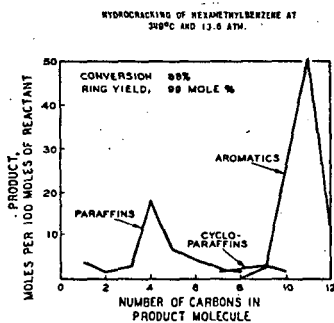
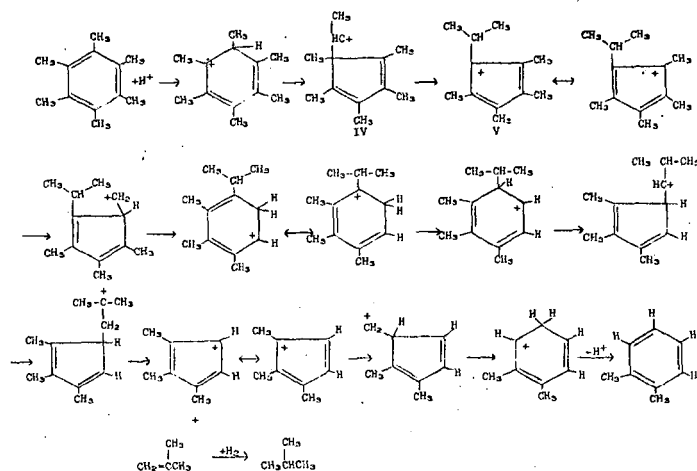


Fig. 4



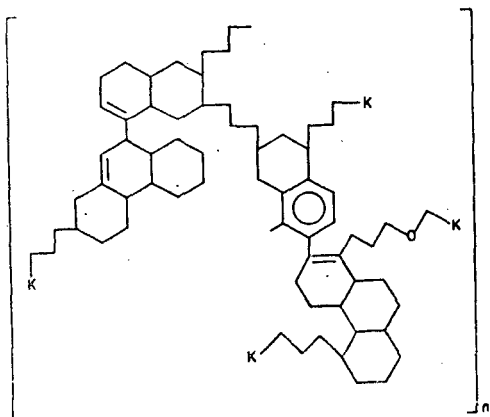
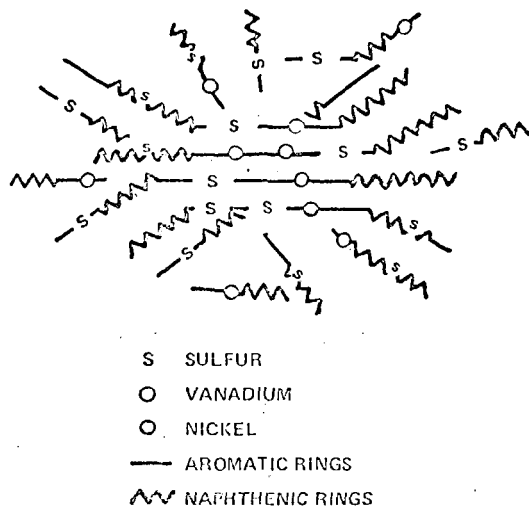


Fig. 6

Generalized Structure of Kerogen of the Green River Formation

Table 1.—United States total gross consumption of energy resources by major sources,¹ 1947-70 revised, and 1971 preliminary

Year	(Trillion Btu)							Percentage change from prior year
	Anthracite	Bituminous coal and lignite	Natural gas dry ²	Petroleum ³	Total fossil fuels	Hydropower ⁴	Nuclear power ⁴	Total gross energy inputs
1947	1,224	14,600	4,518	11,367	31,709	1,326	--	33,035
1948	1,275	13,622	5,033	12,557	32,487	1,393	--	33,880
1949	968	11,673	5,289	12,119	30,039	1,449	--	31,488
1950	1,013	11,900	6,150	13,489	32,552	1,440	--	33,992
1951	940	12,285	7,248	14,848	35,321	1,454	--	36,775
1952	897	10,971	7,760	15,334	34,962	1,496	--	36,458
1953	711	11,182	8,156	16,098	36,147	1,439	--	37,586
1954	683	9,512	8,548	16,132	34,875	1,388	--	36,263
1955	599	10,941	9,232	17,524	38,296	1,407	--	39,703
1956	610	11,142	9,834	18,627	40,213	1,487	--	41,700
1957	528	10,640	10,418	18,570	40,154	1,551	1	41,706
1958	483	9,366	10,995	19,214	40,068	1,636	2	41,696
1959	478	9,332	11,990	19,747	41,547	1,591	2	43,140
1960	447	9,693	12,699	20,067	42,906	1,657	6	44,569
1961	404	9,502	13,228	20,487	43,621	1,680	18	45,319
1962	363	9,826	14,121	21,267	45,577	1,821	24	47,422
1963	361	10,353	14,843	21,950	47,507	1,767	34	49,308
1964	365	10,899	15,648	22,386	49,298	1,907	35	51,240
1965	328	11,580	16,098	23,241	51,247	2,058	38	53,343
1966	290	12,206	17,393	24,394	54,282	2,073	57	56,412
1967	274	11,982	18,250	25,335	55,841	2,344	80	58,265
1968	268	12,401	19,580	27,062	59,291	2,342	130	61,763
1969	224	12,509	21,020	28,421	62,174	2,659	146	64,979
1970	210	12,712	22,029	29,614	64,565	2,650	229	67,444
1971	186	11,857	22,819	30,570	68,698	2,862	404	68,698
1972	150	12,345	23,125	32,966	68,586	2,946	576	72,108
1973	140	13,380	23,558	34,689	71,767	2,941	853	75,561

¹ Gross energy is that contained in all types of commercial energy at the time it is incorporated in the economy, whether the energy is produced domestically or imported. Gross energy comprises inputs of primary fuels (or their derivatives), and outputs of hydropower and nuclear power converted to theoretical energy inputs. Gross energy includes the energy used for the production, processing, and transportation of energy proper.

² Excludes natural gas liquids.

³ Petroleum products including still gas, liquefied refinery gas, and natural gas liquids.

⁴ Outputs of hydropower (adjusted for net imports or net exports) and nuclear power converted to theoretical energy inputs calculated from national average heat rates for fossil-fueled steam-electric plants provided by the Federal Power Commission. Energy input for nuclear power in 1971 is converted at an average heat rate of 10,660 Btu per net kilowatt-hour based on information from the Atomic Energy Commission. Excludes inputs for power generated by nonutility fuel-burning plants, which are included within the other consuming sectors.